Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Facile One-Pot Synthesis of 2-Aminoindoles from Simple Anilines and Ynamides

Young Ho Kim, Huen Ji Yoo, and So Won Youn*

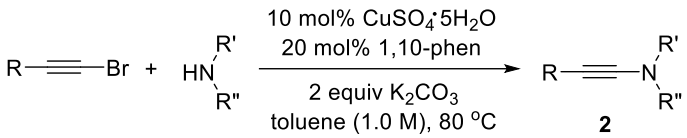
Center for New Directions in Organic Synthesis, Department of Chemistry and Research Institute for Natural Sciences, Hanyang University, Seoul 04763, Korea.

Table of Contents

General Information

Nuclear Magnetic Resonance spectra were recorded on 400 MHz instruments. Spectra were recorded in $CDCl_3$ solutions referenced to TMS or solvent residual peaks. High Resolution Mass Spectra were measured using EI at 70 eV. GC-MS spectra were recorded on a Perkin Elmer's Clarus 600S GC-system with Turbo mass ver. 5.4.2 inert Mass Selective Detector (EI) and Elite-1 column (0.25 mm x 30 m, Film: 0.25 μm). For control of the conversion and characterization of the products, the following method was used: The method starts with the injection temperature T_0 (50 °C), after holding this temperature for 5 min, the column is heated to the temperature T_1 (ramp, 300 °C, 10 °C/min) and hold for additional 10 min. LC-MS spectra were recorded on Agilent Technologies 6120 Quadrupole LC/MS with Open LAB CDS chemstation Edition Rev. C.01.07 SR3 and Poroshell 120 EC-C18 (4.6 x 50 nm, 2.7 μm). Flash chromatography was performed on silica gel 230-400 mesh. All commercially available catalysts and ligands were purchased from Sigma-Aldrich or Strem and used as received. Unless otherwise noted, all commercially obtained reagents and solvents were used as received. Anhydrous toluene, $ClCH_2CH_2Cl$, DMF, and 1,4-dioxane were purchased from Sigma-Aldrich in a SureSeal™ bottle and used as received. THF was distilled from sodium benzophenone ketyl immediately prior to use. Acetone was distilled from $CaSO_4$ immediately prior to use. EtOH and MeCN were distilled from CaH_2 immediately prior to use. Thin layer chromatograms (TLC) was visualized via UV. 1-Bromoalkynes, which are used for ynamide preparation, were synthesized according to literature procedure.[1]

General Procedure for the Preparation of Ynamides (2)[2]



To a solution of the appropriate 1-bromoalkyne (0.709~6.07 mmol, 1.1 equiv) in toluene (0.6~5.5 mL, 1.0 M) were added $CuSO_4 \cdot 5H_2O$ (0.0644~0.552 mmol, 10 mol%), 1,10-phenanthroline (0.129~1.10 mmol, 20 mol%), K_2CO_3 (1.29~11.04 mmol, 2 equiv) and amide (0.644~5.52 mmol, 1.0 equiv) at room temperature under Ar. After being stirred at 80 °C overnight, the reaction mixture was cooled to room temperature, filtered through a pad of Celite, and washed with CH_2Cl_2. The residue was concentrated in vacuo and purified by column chromatography on silica gel to give the corresponding product **2**.

Preparation and spectral data of **2a-e** are available in our previous report.[3]

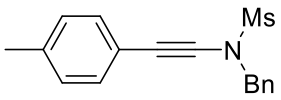
---

[1] Mukherjee, A.; Dateer, R. B.; Chaudhuri, R.; Bhunia, S.; Karad, S. N.; Liu, R.-S. *J. Am. Chem. Soc.* **2011**, *133*, 15372.

[2] (a) Zhang, Y.; Hsung, R. P.; Tracey, M. R.; Kurtz, K. C. M.; Vera, E. L. *Org. Lett.* **2004**, *6*, 1151. (b) Zhang, X.; Zhang, Y.; Huang, J.; Hsung, R. P.; Kurtz, K. C. M.; Oppenheimer, J.; Petersen, M. E.; Sagamanova, I. K.; Shen, L.; Tracey, M. R. *J. Org. Chem.* **2006**, *71*, 4170. (c) Sagamanova, I. K.; Kurtz, K. C. M.; Hsung, R. P. *Org. Synth.* **2007**, *84*, 359.

[3] Yoo, H. J.; Youn, S. W. *Org. Lett.* **2019**, *21*, 3422.

_N_-Benzyl-_N_-(_p_-tolylethynyl)methanesulfonamide (2f)

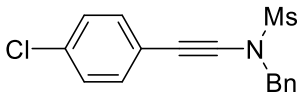


155.6 mg, 85%, a yellow solid (EtOAc : _n_-Hexane = 1:3), mp 78-80 °C.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.49 (dd, J = 7.8, 1.8 Hz, 2H), 7.43-7.37 (m, 3H), 7.26 (d, J = 8.0 Hz, 2H), 7.10 (d, J = 8.0 Hz, 2H), 4.71 (s, 2H), 2.93 (s, 3H), 2.34 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 138.2, 134.6, 131.5, 129.02, 129.00, 128.8, 128.7, 119.3, 81.2, 71.5, 55.9, 38.9, 21.4. EIMS _m/z_ 299 (M^+), 220, 193, 119, 91, 65.

Spectral data were consistent with data reported in the literature.[4a-b]

_N_-Benzyl-_N_-((4-chlorophenyl)ethynyl)methanesulfonamide (2g)

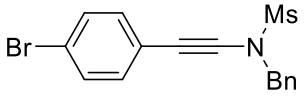


262.3 mg, 82%, a yellow solid (EtOAc : _n_-Hexane = 1:6), mp 65-67 °C.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.48-7.45 (m, 2H), 7.43-7.35 (m, 3H), 7.25 (m, 4H), 4.70 (s, 2H), 2.94 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 134.3, 133.9, 132.5, 128.9, 128.81, 128.78, 128.6, 120.9, 82.8, 70.6, 55.8, 39.1. EIMS _m/z_ 319 (M^+), 252, 240, 205, 178, 139, 114, 65.

Spectral data were consistent with data reported in the literature.[4b-c]

_N_-Benzyl-_N_-((4-bromophenyl)ethynyl)methanesulfonamide (2h)

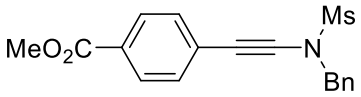


227.8 mg, 96%, a yellow solid (EtOAc : _n_-Hexane = 1:3), mp 104-107 °C.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.49-7.46 (m, 2H), 7.43-7.38 (m, 5H), 7.19 (dt, J = 8.4, 2.2 Hz, 2H), 4.71 (s, 2H), 2.94 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 134.4, 132.7, 131.5, 129.0, 128.9, 128.8, 122.1, 121.4, 83.0, 70.7, 55.8, 39.1. EIMS _m/z_ 365, 363 (M^+), 336, 284, 252, 205, 183, 114, 91, 65.

Spectral data were consistent with data reported in the literature.[4c]

Methyl 4-((_N_-Benzylmethylsulfonamido)ethynyl)benzoate (2i)



211.3 mg, 62%, a yellow solid (EtOAc : _n_-Hexane = 1:3), mp 88-90 °C.

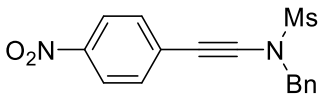
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.94 (d, J = 6.8 Hz, 2H), 7.48 (d, J = 7.6 Hz, 2H), 7.43-7.38 (m, 3H), 7.36 (dd, J = 8.2, 1.0 Hz, 2H), 4.72 (s, 2H), 3.90 (s, 3H), 2.96 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 166.4, 134.2, 130.5, 129.4, 128.91, 128.85, 127.4, 85.1, 71.5, 55.8, 52.1, 39.2 (2 carbons are missing due to overlapping). EIMS _m/z_ 343 (M^+), 264, 252, 232, 179, 158, 114, 91, 65.

Spectral data were consistent with data reported in the literature.[4c]

---

[4] (a) Li, Long.; Zhou, B.; Wang, Y.-H.; Shu, C.; Pan, Y. –F.; Lu, X.; Ye, L.-W. *Angew. Chem. Int. Ed.* **2015**, *54*, 8245. (b) Yao, B.; Liang, Z.; Niu, T.; Zhang, Y. *J. Org. Chem.* **2009**, *74*, 4630. (c) Oh, K. H.; Kim, J. G.; Park, J. K. *Org. Lett.* **2017**, *19*, 3994.

***N*-Benzyl-*N*-((4-nitrophenyl)ethynyl)methanesulfonamide (2j)**

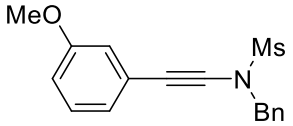


137.4 mg, 63%, a yellow oil ((EtOAc : *n*-Hexane = 1:2).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.14 (d, J = 8.8 Hz, 2H), 7.48-7.39 (m, 7H), 4.75 (s, 2H), 2.99 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 146.4, 134.0, 130.9, 129.8, 129.04, 128.98, 128.9, 123.6, 87.6, 71.3, 55.9, 39.6. EIMS *m*/*z* 330 (M^+), 281, 252, 207, 91, 65.

Spectral data were consistent with data reported in the literature.[5]

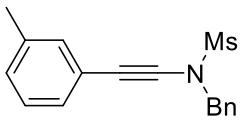
***N*-Benzyl-*N*-((3-methoxyphenyl)ethynyl)methanesulfonamide (2k)**



45.2 mg, 67%, a brown oil (EtOAc : *n*-Hexane = 1:3).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.50 (dd, J = 8.0, 1.2 Hz, 2H), 7.44-7.38 (m, 3H), 7.20 (t, J = 7.8 Hz, 1H), 6.95 (dd, J = 7.6, 0.8 Hz, 1H), 6.87 (d, J = 0.4 Hz, 1H), 6.85 (dd, J = 8.2, 2.6 Hz, 1H), 4.71 (s, 2H), 3.78 (s, 3H), 2.95 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 159.3, 134.5, 129.3, 129.0, 128.8, 128.7, 123.8, 123.5, 116.2, 114.4, 81.8, 71.6, 55.9, 55.2, 39.0. LCMS *m*/*z* 316 $[M+H]^+$. HRMS (EI) $[M]^+$ *m*/*z* calcd for $C_{17}H_{17}NO_3S$ 315.0924, found 315.0931.

***N*-Benzyl-*N*-(*m*-tolylethynyl)methanesulfonamide (2l)**

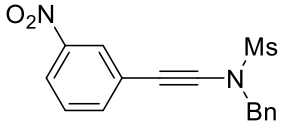


324.2 mg, 83%, a yellow oil (EtOAc : *n*-Hexane = 1:3).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.50 (dd, J = 7.8, 1.8 Hz, 2H), 7.44-7.36 (m, 3H), 7.20-7.15 (m, 3H), 7.13-7.09 (m, 1H), 4.71 (s, 2H), 2.93 (s, 3H), 2.32 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 138.0, 134.5, 132.0, 129.0, 128.9, 128.8, 128.7, 128.4, 128.2, 122.2, 81.6, 71.7, 55.9, 38.9, 21.2. EIMS *m*/*z* 299 (M^+), 252, 220, 193, 178, 128, 119, 103, 77, 65.

Spectral data were consistent with data reported in the literature.[4c]

***N*-Benzyl-*N*-((3-nitrophenyl)ethynyl)methanesulfonamide (2m)**



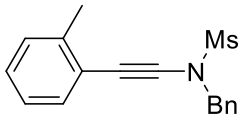
601.2 mg, 82%, a yellow oil (EtOAc : *n*-Hexane = 1:3).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.13 (s, 1H), 8.11 (d, J = 8.4 Hz, 1H), 7.60 (d, J = 7.6 Hz, 1H), 7.49-7.38 (m, 6H), 4.74 (s, 2H), 2.99 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 148.0, 136.6, 134.1, 129.3, 128.98, 128.95, 128.9, 125.6, 124.4, 122.4, 84.5, 70.0, 55.8, 39.4. EIMS *m*/*z* 330 (M^+), 251, 219, 207, 176, 150,

[5] Tracer, M. R.; Zhang, Y.; Frederick, M. O.; Mulder, J. A.; Hsung, R. P. *Org. Lett.* **2004**, *6*, 2209.

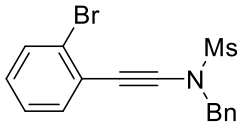
114, 91, 78, 65. HRMS (EI) $[M]^+$ *m/z* calcd for $C_{16}H_{14}N_2O_4S$ 330.0669, found 330.0670.

_N_-Benzyl-_N_-(_o_-tolylethynyl)methanesulfonamide (2n)



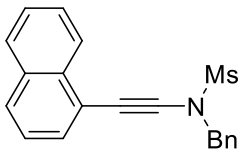
151.3 mg, 72%, a yellow solid (EtOAc : *n*-Hexane = 1:6), mp 38-40 °C.
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.50 (d, J = 7.2 Hz, 2H), 7.43-7.35 (m, 3H), 7.31 (d, J = 7.2 Hz, 1H), 7.20-7.16 (m, 2H), 7.11 (td, J = 6.9, 2.4 Hz, 1H), 4.73 (s, 2H), 2.96 (s, 3H), 2.30 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 139.7, 134.5, 131.4, 129.4, 129.0, 128.8, 128.7, 127.9, 125.5, 122.2, 85.7, 70.7, 55.9, 38.8, 20.6. EIMS *m/z* 299 (M^+), 252, 220, 204, 193, 178, 119, 91, 77, 65.
Spectral data were consistent with data reported in the literature.[4c]

_N_-Benzyl-_N_-((2-bromophenyl)ethynyl)methanesulfonamide (2o)



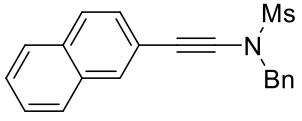
496.6 mg, 69%, a white solid (EtOAc : *n*-Hexane = 1:5), mp 84-86 °C.
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.57-7.54 (m, 3H), 7.43-7.38 (m, 3H), 7.36 (dd, J = 8.0, 1.6 Hz, 1H), 7.23 (td, J = 7.6, 1.2 Hz, 1H), 7.12 (td, J = 7.8, 1.6 Hz, 1H), 4.75 (s, 2H), 2.97 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 134.4, 132.6, 132.3, 129.1, 128.9, 128.84, 128.80, 127.0, 125.0, 124.8, 86.5, 70.9, 55.9, 39.2. LCMS *m/z* 366, 364 $[M+H]^+$.
Spectral data were consistent with data reported in the literature.[6]

_N_-Benzyl-_N_-(naphthalen-1-ylethynyl)methanesulfonamide (2p)



436.4 mg, 73%, a yellow solid (EtOAc : *n*-Hexane = 1:4), mp 66-68 °C.
^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.03-8.00 (m, 1H), 7.83-7.81 (m, 1H), 7.78 (d, J = 8.0 Hz, 1H), 7.58-7.55 (m, 3H), 7.51-7.38 (m, 6H), 4.81 (s, 2H), 3.04 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 134.5, 133.11, 133.05, 129.6, 129.1, 128.9, 128.8, 128.3, 128.2, 126.7, 126.3, 126.0, 125.1, 120.1, 86.4, 70.2, 55.9, 39.0. EIMS *m/z* 335 (M^+), 252, 229, 178, 91, 65. HRMS (EI) $[M]^+$ *m/z* calcd for $C_{20}H_{17}NO_2S$ 335.0975, found 335.0981.

_N_-Benzyl-_N_-(naphthalen-2-ylethynyl)methanesulfonamide (2q)



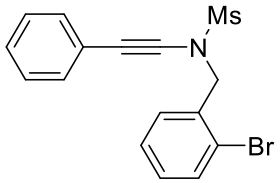
175.3 mg, 54%, a yellow solid (EtOAc : *n*-Hexane = 1:5), mp 114-116 °C.

---

[6] Garzón, M.; Davies, P. W. *Org. Lett.* **2014**, *16*, 4850.

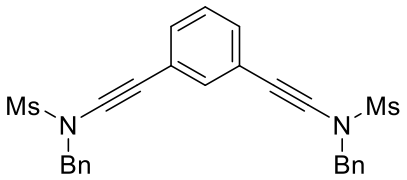
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.87 (s, 1H), 7.81-7.74 (m, 3H), 7.53 (d, J = 7.2 Hz, 2H), 7.51-7.38 (m, 6H), 4.76 (s, 2H), 2.98 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 134.5, 132.9, 132.6, 131.0, 129.0, 128.9, 128.8, 128.2, 127.9, 127.7, 127.6, 126.5, 119.7, 82.3, 72.0, 56.0, 39.1 (1 carbon is missing due to overlapping). EIMS *m*/*z* 335 (M^+), 252, 207, 155, 127, 91, 65.
Spectral data were consistent with data reported in the literature.[7]

_N_-(2-Bromobenzyl)-_N_-(phenylethynyl)methanesulfonamide (2r)



1.0 g, 87%, a yellow solid (EtOAc : *n*-Hexane = 1:6), mp 97-99 °C.
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.62 (dd, J = 8.0, 1.2 Hz, 1H), 7.60 (dd, J = 7.8, 1.6 Hz, 1H), 7.39 (td, J = 7.6, 1.2 Hz, 1H), 7.32-7.26 (m, 5H), 7.24 (td, J = 7.8, 1.4 Hz, 1H), 4.88 (s, 2H), 3.21 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 133.9, 133.0, 131.1, 130.7, 130.0, 128.2, 127.9, 127.8, 123.8, 122.3, 81.4, 71.7, 55.0, 38.8. EIMS *m*/*z* 365, 363 (M^+), 284, 252, 235, 205, 169, 115, 105, 89, 77, 63. HRMS (EI) $[M]^+$ *m*/*z* calcd for $C_{16}H_{14}BrNO_2S$ 362.9923, found 362.9936.

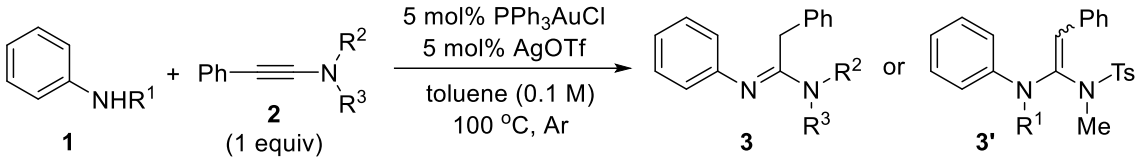
_N_,_N_′-(1,3-Phenylenebis(ethyne-2,1-diyl))bis(_N_-benzylmethanesulfonamide) (2s)



821.6 mg, 80%, a white solid (EtOAc : *n*-Hexane = 1:2), mp 84-86 °C.
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.48 (dd, J =7.8, 1.8 Hz, 4H), 7.44-7.37 (m, 6H), 7.34 (s, 1H), 7.26-7.52 (m, 1H), 7.24-7.19 (m, 2H), 4.71 (s, 4H), 2.94 (s, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 134.3, 133.7, 130.5, 128.9, 128.81, 128.76, 128.3, 122.7, 82.6, 70.8, 55.8, 39.0. LCMS *m*/*z* 493 $[M+H]^+$, 494 $[M+2H]^+$. HRMS (EI) $[M]^+$ *m*/*z* calcd for $C_{26}H_{24}N_2O_4S_2$ 492.1172, found 492.1177.

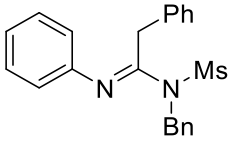
[7] Lu, Z.; Kong, W.; Yuan, Z.; Zhao, X.; Zhu, G. *J. Org. Chem.* **2011**, *76*, 8524.

General Procedure for the Au(I)-Catalyzed Hydroamination of Ynamides with Anilines



To a solution of the substrate **1** (0.110~0.325 mmol, 1 equiv) and **2** (0.110~0.325 mmol, 1 equiv) in toluene (1.1~3.3 mL, 0.1 M) were added PPh_3AuCl (0.00548~0.0163 mmol, 5 mol%) and AgOTf (0.00548~0.0163 mmol, 5 mol%). After being stirred at 100 °C for the reported time under Ar, the reaction mixture was concentrated in vacuo. The residue was purified by column chromatography on silica gel to give the corresponding product **3**. All reactions were carried out 2-3 times repetitively and the average values of yields are given.

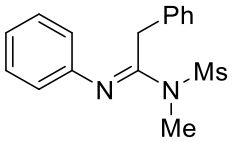
(*E*)-*N*-Benzyl-*N*-(methylsulfonyl)-*N′*,2-diphenylacetimidamide (3aa)



85% (108.8 mg), 2 h. a yellow solid (EtOAc : *n*-Hexane = 1:8), mp 90-92 °C.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.33-7.18 (m, 10H), 7.06-7.00 (m, 3H), 6.73 (dd, J = 8.4, 0.8 Hz, 2H), 4.84 (s, 2H), 3.81 (s, 2H), 3.08 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 156.0, 147.9, 136.5, 134.5, 129.1, 128.7, 128.60, 128.56, 127.9, 127.7, 126.9, 123.7, 119.7, 50.0, 41.7, 36.3. LCMS *m*/*z* 379 $[M+H]^+$. HRMS (EI) $[M]^+$ *m/z* calcd for $C_{22}H_{22}N_2O_2S$ 378.1397, found 378.1401.

(*E*)-*N*-Methyl-*N*-(methylsulfonyl)-*N′*,2-diphenylacetimidamide (3ab)

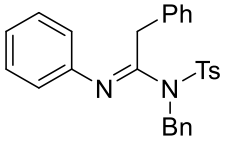


85% (33.8 mg), 2 h. a colorless oil (EtOAc : *n*-Hexane = 1:6).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.33-7.28 (m, 4H), 7.24 (t, J = 7.6 Hz, 1H), 7.17 (d, J = 7.2 Hz, 2H), 7.07 (t, J = 7.4 Hz, 1H), 6.81 (d, J = 7.6 Hz, 2H), 3.95 (s, 2H), 3.18 (s, 3H), 2.95 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 156.9, 148.0, 135.1, 129.2, 128.8, 128.5, 127.0, 123.7, 120.0, 40.0, 36.2, 34.7. LCMS *m*/*z* 303 $[M+H]^+$.

Spectral data were consistent with data reported in the literature.[1]

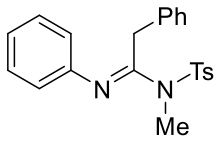
(*E*)-*N*-Benzyl-*N′*,2-diphenyl-*N*-tosylacetimidamide (3ac)



80% (199.7 mg), 3 h. a white solid (EtOAc : *n*-Hexane = 1:8), mp 94-96 °C.

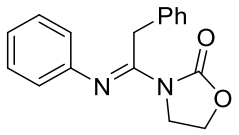
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.77 (d, J = 8.4 Hz, 2H), 7.36 (d, J = 8.0 Hz, 2H), 7.27-7.21 (m, 3H), 7.19-7.15 (m, 3H), 7.11 (t, J = 7.2 Hz, 2H), 7.06-7.01 (m, 3H), 6.81 (d, J = 7.2 Hz, 2H), 6.45 (d, J = 7.2 Hz, 2H), 4.69 (s, 2H), 3.91 (s, 2H), 2.48 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 155.6, 148.0, 144.1, 135.8, 135.4, 134.7, 129.5, 129.1, 129.0, 128.8, 128.3, 128.1, 128.0, 127.2, 126.4, 123.5, 119.4, 51.0, 37.7, 21.6. LCMS *m*/*z* 455 $[M+H]^+$. HRMS (EI) $[M]^+$ *m/z* calcd for $C_{28}H_{26}N_2O_2S$ 454.1710, found 474.1715.

(*E*)-*N*-Methyl-*N′*,2-diphenyl-*N*-tosylacetimidamide (3ad)



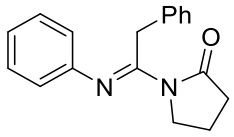
90% (217.7 mg), 1 h. a pale yellow solid (EtOAc : *n*-Hexane = 1:5), mp 108-110 °C.
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.64 (d, J = 8.4 Hz, 2H), 7.29-7.21 (m, 7H), 7.07 (d, J = 6.8 Hz, 2H), 7.04 (t, J = 7.4 Hz, 1H), 6.62 (d, J = 7.6 Hz, 2H), 4.04 (s, 2H), 3.10 (s, 3H), 2.43 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 157.5, 148.1, 144.0, 135.7, 135.1, 129.4, 129.0, 128.61, 128.58, 127.9, 126.6, 123.6, 119.8, 37.1, 35.7, 21.6. LCMS *m*/*z* 379 $[M+H]^+$. HRMS (EI) $[M]^+$ *m/z* calcd for $C_{22}H_{22}N_2O_2S$ 378.1397, found 378.1404.

(*E*)-3-(2-Phenyl-1-(phenylimino)ethyl)oxazolidin-2-one (3ae)



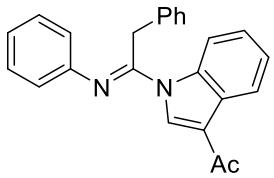
85% (57.7 mg), 2 h. a colorless oil (EtOAc : *n*-Hexane = 1:4).
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.26 (tt, J = 7.6, 1.8 Hz, 2H), 7.21 (tt, J = 7.2, 1.6 Hz, 2H), 7.15 (tt, J = 7.2, 1.2 Hz, 1H), 7.07 (dd, J = 7.2, 1.2 Hz, 2H), 7.03 (tt, J = 7.4, 1.0 Hz, 1H), 6.75 (dd, J = 8.4, 1.2 Hz, 2H), 4.29 (t, J = 8.0 Hz, 2H), 4.25 (s, 2H), 4.10 (t, J = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 154.7, 154.0, 147.7, 136.0, 129.0, 128.4, 126.4, 123.5, 120.6, 61.7, 44.7, 33.2 (1 carbon is missing due to overlapping). LCMS *m*/*z* 281 $[M+H]^+$. HRMS (EI) $[M]^+$ *m/z* calcd for $C_{17}H_{16}N_2O_2$ 280.1206, found 280.1212.

(*E*)-1-(2-Phenyl-1-(phenylimino)ethyl)pyrrolidin-2-one



67% (108.7 mg), 4 h. a colorless oil (only EtOAc).
^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.05 (dd, J = 7.6, 1.6 Hz, 2H), 7.58 (tt, J = 7.4, 1.2 Hz, 1H), 7.48 (td, J = 7.6, 1.6 Hz, 2H), 7.22 (td, J = 7.8, 1.8 Hz, 2H), 6.95 (tt, J = 7.4, 1.2 Hz, 1H), 6.81 (dd, J = 8.2, 1.0 Hz, 2H), 4.91 (s, 2H), 3.47 (t, J = 6.8 Hz, 2H), 2.46 (t, J = 7.8 Hz, 2H), 2.01 (quintet, J = 7.3 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 195.3, 162.3, 152.2, 135.4, 133.5, 128.7, 128.6, 128.1, 122.2, 121.9, 50.6, 49.4, 27.1, 20.2. LCMS *m*/*z* 279 $[M+H]^+$. HRMS (EI) $[M]^+$ *m/z* calcd for $C_{18}H_{18}N_2O$ 278.1414, found 278.1416.

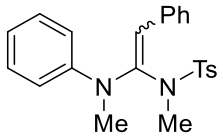
(*E*)-1-(1-(2-Phenyl-1-(phenylimino)ethyl)-1*H*-indol-3-yl)ethan-1-one



72% (134.0 mg), 3 h. a yellow solid (EtOAc : *n*-Hexane = 1:3), mp 138-140 °C.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.79-8.76 (m, 1H), 8.40-8.38 (m, 1H), 7.97 (s, 1H), 7.42-7.36 (m, 4H), 7.32 (t, J = 7.2 Hz, 2H), 7.25 (t, J = 7.4 Hz, 1H), 7.19 (d, J = 7.2 Hz, 2H), 7.15 (t, J = 7.4 Hz, 1H), 6.97 (d, J = 8.0 Hz, 2H), 4.27 (s, 2H), 2.38 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 193.3, 152.9, 147.8, 136.5, 134.9, 132.6, 129.3, 127.6, 127.3, 127.2, 125.3, 124.4, 124.0, 122.2, 119.9, 116.9, 35.8, 27.5 (2 carbons are missing due to overlapping). LCMS *m*/*z* 353 $[M+H]^+$. HRMS (EI) $[M]^+$ *m/z* calcd for $C_{24}H_{20}N_2O$ 352.1570, found 352.1570.

***N*,4-Dimethyl-*N*-(1-(methyl(phenyl)amino)-2-phenylvinyl)benzenesulfonamide (3′-Me)**

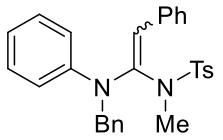


85% (69.1 mg), 3 h. a white solid (EtOAc : *n*-Hexane = 1:8), mp 125-127 °C.

Stereochemistry of olefin could not be determined and *E*/*Z* mixture was obtained with a 1:10 (= **A** : **B**) ratio.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.59 (d, J = 7.2 Hz, 2H of **A** & 2H of **B**), 7.49 (d, J = 7.6 Hz, 2H of **A**), 7.36 (t, J = 7.6 Hz, 2H of **A**), 7.23-7.12 (m, 4H of **A** & 9H of **B**), 7.06 (d, J = 8.4 Hz, 2H of **A**), 6.90 (t, J = 7.2 Hz, 2H of **A**), 6.86 (t, J = 7.2 Hz, 1H of **B**), 6.81 (d, J = 8.4 Hz, 2H of **B**), 5.84 (s, 1H of **A**), 5.75 (s, 1H of **B**), 3.15 (s, 3H of **B**), 3.08 (s, 3H of **A** & 3H of **B**), 2.67 (s, 3H of **A**), 2.43 (s, 3H of **B**), 2.38 (s, 3H of **A**). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 147.4, 145.4, 143.8, 143.4, 143.0, 141.3, 137.2, 135.4, 134.8, 129.2, 129.1, 128.70, 128.65, 128.4, 128.3, 127.6, 127.3, 127.2, 127.0, 126.8, 126.6, 120.4, 119.5, 117.7, 115.8, 115.0, 114.9, 38.1, 37.8, 37.7, 36.9, 21.41, 21.36 (1 carbon is missing due to overlapping). LCMS *m*/*z* 393 $[M+H]^+$. HRMS (EI) $[M]^+$ *m/z* calcd for $C_{23}H_{24}N_2O_2S$ 392.1553, found 392.1554.

***N*-(1-(Benzyl(phenyl)amino)-2-phenylvinyl)-*N*,4-dimethylbenzenesulfonamide (3′-Bn)**



Total 72% (55.6 mg), 3 h. Stereochemistry of olefin could not be determined and *E*/*Z* mixture was obtained with a 1.1:1 (= **A** : **B**) ratio.

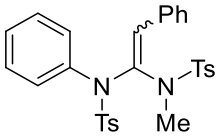
A isomer: 38% (29.4 mg), a colorless oil (EtOAc : *n*-Hexane = 1:8).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.51 (d, J = 8.4 Hz, 2H), 7.45 (d, J = 7.6 Hz, 2H), 7.32 (td, J = 7.8, 2.0 Hz, 2H), 7.27 (dd, J = 7.2, 1.2 Hz, 2H), 7.22-7.17 (m, 4H), 7.14-7.10 (m, 4H), 7.00 (dd, J = 8.8, 0.8 Hz, 2H), 6.82 (tt, J = 7.4, 1.0 Hz, 1H), 6.17 (s, 1H), 4.40 (s, 2H), 2.93 (s, 3H), 2.39 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 146.7, 143.3, 141.7, 138.8, 136.8, 134.7, 129.3, 128.8, 128.5, 127.9, 127.1, 126.8, 126.74, 126.71, 120.2, 117.8, 116.2, 53.0, 37.7, 21.5 (1 carbon is missing due to overlapping). LCMS *m*/*z* 469 $[M+H]^+$. HRMS (EI) $[M]^+$ *m/z* calcd for $C_{29}H_{28}N_2O_2S$ 468.1866, found 468.1870.

B isomer: 34% (26.2 mg), a colorless oil (EtOAc : *n*-Hexane = 1:8).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.76 (d, J = 8.0 Hz, 2H), 7.36-7.27 (m, 6H), 7.25-7.22 (m, 1H), 7.10-6.98 (m, 9H), 6.75 (tt, J = 7.2, 1.0 Hz, 1H), 5.67 (s, 1H), 4.80 (s, 2H), 2.91 (s, 3H), 2.46 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 145.5, 143.8, 139.0, 138.6, 135.4, 134.2, 129.6, 128.7, 128.4, 128.02, 127.95, 127.8, 127.7, 127.0, 126.7, 120.4, 117.5, 115.2, 53.8, 37.0, 21.6. LCMS *m*/*z* 469 $[M+H]^+$. HRMS (EI) $[M]^+$ *m*/*z* calcd for $C_{29}H_{28}N_2O_2S$ 468.1866, found 468.1872.

_N_-(1-((_N_,4-Dimethylphenyl)sulfonamido)-2-phenylvinyl)-4-methyl-_N_-phenylbenzenesulfonamide (3′-Ts)

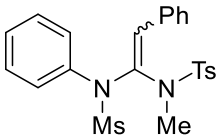


45% (49.8 mg), 3 h. a colorless oil (EtOAc : *n*-Hexane = 1:6).

Stereochemistry of olefin could not be determined and only one isomer was obtained.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.48 (d, J = 8.0 Hz, 2H), 7.38-7.33 (m, 3H), 7.32-7.23 (m, 9H), 7.05 (d, J = 8.4 Hz, 2H), 6.99 (d, J = 8.4 Hz, 2H), 6.25 (s, 1H), 3.08 (s, 3H), 2.44 (s, 3H), 2.35 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 144.0, 142.9, 137.8, 136.5, 135.8, 133.9, 132.7, 129.5, 129.2, 129.0, 128.8, 128.5, 128.4, 128.3, 128.1, 128.0, 127.5, 35.1, 21.6, 21.4 (1 carbon is missing due to overlapping). LCMS *m*/*z* 533 $[M+H]^+$. HRMS (EI) $[M]^+$ *m*/*z* calcd for $C_{29}H_{28}N_2O_4S_2$ 532.1485, found 532.1491.

_N_,4-Dimethyl-_N_-(2-phenyl-1-(_N_-phenylmethylsulfonamido)vinyl)benzenesulfonamide (3′-Ms)



Total 50% (74.0 mg), 3 h. Stereochemistry of olefin could not be determined and *E*/*Z* mixture was obtained with a 1.7:1 (= **A** : **B**) ratio.

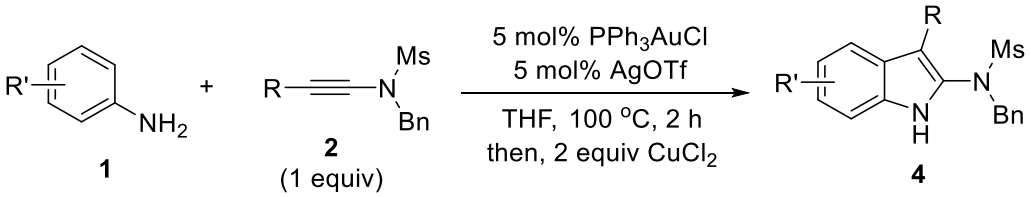
A isomer: 31% (46.5 mg), a colorless oil (EtOAc : *n*-Hexane = 1:6).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.41-7.38 (m, 2H), 7.33-7.30 (m, 5H), 7.26-7.24 (m, 2H), 7.22-7.19 (m, 3H), 7.09 (d, J = 8.0 Hz, 2H), 6.69 (s, 1H), 3.17 (s, 3H), 2.85 (s, 3H), 2.35 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 143.5, 137.4, 136.2, 133.8, 133.3, 129.4, 129.3, 129.0, 128.54, 128.48, 128.4, 128.3, 127.4, 126.6, 39.9, 36.7, 21.4. LCMS *m*/*z* 457 $[M+H]^+$. HRMS (EI) $[M]^+$ *m*/*z* calcd for $C_{23}H_{24}N_2O_4S_2$ 456.1172, found 456.1174.

B isomer: 19% (27.5 mg), a colorless oil (EtOAc : *n*-Hexane = 1:6).

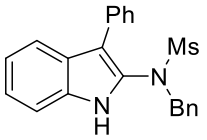
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.67 (d, J = 8.4 Hz, 2H), 7.60-7.57 (m, 2H), 7.33-7.24 (m, 10H), 5.83 (s, 1H), 3.08 (s, 3H), 2.90 (s, 3H), 2.46 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 144.2, 138.2, 135.4, 133.9, 133.4, 129.5, 129.1, 128.5, 128.4, 128.30, 128.25, 127.7, 127.5, 126.7, 40.7, 39.2, 21.6. LCMS *m*/*z* 457 $[M+H]^+$. HRMS (EI) $[M]^+$ *m*/*z* calcd for $C_{23}H_{24}N_2O_4S_2$ 456.1172, found 456.1176.

General Procedure for the One-Pot Synthesis of 2-Aminoindoles (4)



To a solution of the substrate **1** (0.104~1.94 mmol, 1 equiv) and **2** (0.104~1.94 mmol, 1 equiv) in THF (1.0~19.4 mL, 0.1 M) were added PPh_3AuCl (0.00520~0.0967 mmol, 5 mol%) and AgOTf (0.00520~0.0967 mmol, 5 mol%). The resulting mixture was stirred at 100 °C for 2 h under Ar. After the reaction mixture was cooled to room temperature, $CuCl_2$ (0.208~3.87 mmol, 2 equiv) was added to the reaction mixture. After being stirred at 100 °C for the reported time under Ar, the reaction mixture was filtered through Celite and concentrated in vacuo. The residue was purified by column chromatography on silica gel to give the corresponding product **4**. All reactions were carried out 3-5 times repetitively and the average values of yields are given.

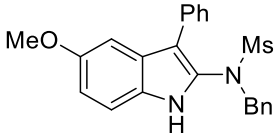
N-Benzyl-*N*-(3-phenyl-1*H*-indol-2-yl)methanesulfonamide (4aa)



73% (54.4 mg), a white solid (EtOAc : *n*-Hexane = 1:3), mp 164-166 °C.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.22 (br s, 1H), 7.61 (d, J = 8.0 Hz, 1H), 7.52-7.46 (m, 4H), 7.42-7.37 (m, 1H), 7.27-7.24 (m, 5H), 7.23-7.20 (m, 2H), 7.12 (ddd, J = 8.0, 6.0, 2.0 Hz, 1H), 4.72 (s, 2H), 2.85 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 136.3, 133.5, 133.4, 129.3, 128.9, 128.72, 128.66, 128.2, 128.1, 127.2, 126.3, 123.4, 120.4, 119.7, 113.4, 111.2, 54.9, 40.1. HRMS (EI) $[M+Na]^+$ *m/z* calcd for $C_{22}H_{20}N_2NaO_2S$ 399.1138, found 399.1141.

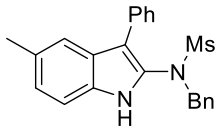
N-Benzyl-*N*-(5-methoxy-3-phenyl-1*H*-indol-2-yl)methanesulfonamide (4ba)



62% (35.3 mg), a yellow solid (EtOAc : *n*-Hexane = 1:4), mp 155-157 °C.

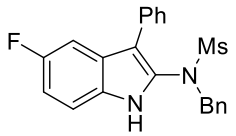
^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.07 (br s, 1H), 7.52-7.43 (m, 4H), 7.40 (tt, J = 7.0, 1.7 Hz, 1H), 7.29-7.25 (m, 3H), 7.22-7.19 (m, 2H), 7.14 (d, J = 8.8 Hz, 1H), 7.03 (d, J = 2.4 Hz, 1H), 6.89 (dd, J = 9.0, 2.6 Hz, 1H), 4.69 (s, 2H), 3.78 (s, 3H), 2.83 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 154.7, 136.3, 133.6, 129.2, 129.0, 128.74, 128.67, 128.6, 128.5, 128.2, 127.2, 126.7, 113.8, 113.3, 112.1, 101.2, 55.9, 55.0, 40.1. HRMS (EI) $[M+Na]^+$ *m/z* calcd for $C_{23}H_{22}N_2NaO_3S$ 429.1243, found 429.1246.

***N*-Benzyl-*N*-(5-methyl-3-phenyl-1*H*-indol-2-yl)methanesulfonamide (4ca)**



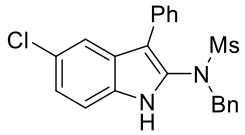
68% (30.9 mg), a white solid (EtOAc : *n*-Hexane = 1:4), mp 144-146 °C.
^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.10 (br s, 1H), 7.51-7.45 (m, 4H), 7.41-7.38 (m, 2H), 7.26-7.25 (m, 3H), 7.22-7.19 (m, 2H), 7.14 (d, J = 8.4 Hz, 1H), 7.05 (dd, J = 8.2, 1.4 Hz, 1H), 4.70 (s, 2H), 2.84 (s, 3H), 2.40 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 136.3, 133.5, 131.7, 129.8, 129.3, 128.9, 128.73, 128.65, 128.2, 127.2, 126.5, 125.0, 119.2, 113.0, 110.9, 54.9, 40.1, 21.5 (1 carbon is missing due to overlapping). HRMS (EI) $[M+Na]^+$ *m/z* calcd for $C_{23}H_{22}N_2NaO_2S$ 413.1294, found 413.1296.

***N*-Benzyl-*N*-(5-fluoro-3-phenyl-1*H*-indol-2-yl)methanesulfonamide (4da)**



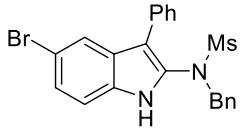
61% (37.3 mg), a white solid (EtOAc : *n*-Hexane = 1:3), mp 180-182 °C.
^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.27 (br s, 1H), 7.49 (t, J = 7.4 Hz, 2H), 7.44-7.38 (m, 3H), 7.26-7.24 (m, 3H), 7.22-7.17 (m, 3H), 7.13 (dd, J = 8.8, 4.4 Hz, 1H), 6.95 (td, J = 9.1, 2.5 Hz, 1H), 4.69 (s, 2H), 2.85 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 158.3 (d, J = 235 Hz), 136.1, 133.0, 129.9, 129.5, 129.1 (d, J = 5 Hz), 128.7, 128.2, 127.5, 126.7 (d, J = 9 Hz), 113.6 (d, J = 5 Hz), 112.1, 111.9 (d, J = 27 Hz), 104.6 (d, J = 24 Hz), 54.8, 40.2 (2 carbons are missing due to overlapping). HRMS (EI) $[M+Na]^+$ *m/z* calcd for $C_{22}H_{19}FN_2NaO_2S$ 417.1043, found 417.1046.

***N*-Benzyl-*N*-(5-chloro-3-phenyl-1*H*-indol-2-yl)methanesulfonamide (4ea)**



66% (40.3 mg), a yellow solid (EtOAc : *n*-Hexane = 1:3), mp 173-175 °C.
^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.28 (br s, 1H), 7.54 (s, 1H), 7.51 (t, J = 7.6 Hz, 2H), 7.44-7.40 (m, 3H), 7.26-7.25 (m, 3H), 7.19-7.13 (m, 4H), 4.69 (s, 2H), 2.87 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 136.0, 132.7, 131.7, 129.2, 129.1, 128.71, 128.67, 128.3, 127.6, 127.4, 126.3, 123.8, 119.1, 113.1, 112.3, 54.8, 40.2 (1 carbon is missing due to overlapping). HRMS (EI) $[M+Na]^+$ *m/z* calcd for $C_{22}H_{19}ClN_2NaO_2S$ 433.0748, found 433.0749.

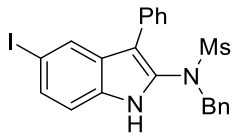
***N*-Benzyl-*N*-(5-bromo-3-phenyl-1*H*-indol-2-yl)methanesulfonamide (4fa)**



87% (684.0 mg), using 1.73 mmol of **1f** and **2a**, a white solid (EtOAc : *n*-Hexane = 1:3), mp 190-192 °C.
^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.31 (br s, 1H), 7.69 (s, 1H), 7.51 (t, J = 7.4 Hz, 2H), 7.43-7.40 (m, 3H), 7.30-7.25 (m, 4H), 7.18-7.17 (m, 2H), 7.10 (dd, J = 8.6, 1.4 Hz, 1H), 4.68 (s, 2H), 2.87 (s, 3H). ^{13}C NMR

($CDCl_3$, 100 MHz) δ 136.0, 132.7, 131.9, 129.2, 129.1, 128.72, 128.67, 128.3, 128.0, 127.6, 126.3, 122.2, 113.8, 113.0, 112.7, 54.7, 40.2 (1 carbon is missing due to overlapping). HRMS (EI) $[M+Na]^+$ *m/z* calcd for $C_{22}H_{19}BrN_2NaO_2S$ 477.0243, found 477.0247.

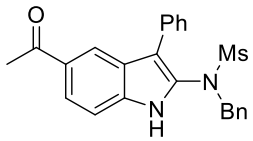
_N_-Benzyl-_N_-(5-iodo-3-phenyl-1_H_-indol-2-yl)methanesulfonamide (4ga)



75% (46.7 mg), a white solid (EtOAc : *n*-Hexane = 1:4), mp 183-185 °C.

^1H NMR ($CDCl_3$, 400 MHz) δ 8.26 (br s, 1H), 7.89 (d, J = 1.6 Hz, 1H), 7.53-7.49 (m, 2H), 7.46 (dd, J = 8.4, 1.6 Hz, 1H), 7.43-7.40 (m, 3H), 7.26-7.22 (m, 3H), 7.18-7.15 (m, 2H), 7.01 (d, J = 8.8 Hz, 1H), 4.67 (s, 2H), 2.87 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 136.0, 132.6, 132.3, 131.7, 129.3, 129.1, 128.8, 128.71, 128.66, 128.4, 128.3, 127.6, 113.2, 112.7, 83.9, 54.7, 40.2 (1 carbon is missing due to overlapping). HRMS (EI) $[M]^+$ *m/z* calcd for $C_{22}H_{19}IN_2O_2S$ 502.0206, found 502.0206.

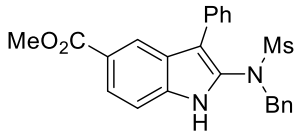
_N_-(5-Acetyl-3-phenyl-1_H_-indol-2-yl)-_N_-benzylmethanesulfonamide (4ha)



56% (24.6 mg), a yellow oil (EtOAc : *n*-Hexane = 1:2).

^1H NMR ($CDCl_3$, 400 MHz) δ 8.46 (br s, 1H), 8.22 (s, 1H), 7.87 (d, J = 8.8 Hz, 1H), 7.54 (t, J = 7.4 Hz, 2H), 7.47-7.45 (m, 3H), 7.26-7.25 (m, 4H), 7.19-7.18 (m, 2H), 4.69 (s, 2H), 2.89 (s, 3H), 2.60 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 198.0, 136.0, 135.9, 132.5, 130.4, 129.4, 129.3, 129.1, 128.72, 128.65, 128.3, 127.8, 126.0, 123.6, 121.7, 115.1, 111.1, 54.8, 40.3, 26.6. HRMS (EI) $[M+Na]^+$ *m/z* calcd for $C_{24}H_{22}N_2NaO_3S$ 441.1243, found 441.1245.

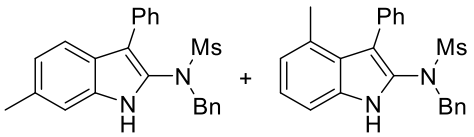
Methyl 2-(_N_-Benzylmethylsulfonamido)-3-phenyl-1_H_-indole-5-carboxylate (4ia)



61% (28.9 mg), a yellow solid (EtOAc : *n*-Hexane = 1:2), mp 158-160 °C.

^1H NMR ($CDCl_3$, 400 MHz) δ 8.40 (br s, 1H), 8.32 (s, 1H), 7.91 (dd, J = 8.4, 1.6 Hz, 1H), 7.53 (t, J = 7.6 Hz, 2H), 7.47-7.43 (m, 3H), 7.26-7.23 (m, 4H), 7.20-7.17 (m, 2H), 4.69 (s, 2H), 3.89 (s, 3H), 2.88 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 167.8, 136.0, 135.9, 132.6, 129.4, 129.2, 129.1, 128.72, 128.66, 128.3, 127.7, 126.0, 124.7, 122.7, 122.6, 114.7, 110.9, 54.8, 51.9, 40.3. HRMS (EI) $[M+Na]^+$ *m/z* calcd for $C_{24}H_{22}N_2NaO_4S$ 457.1192, found 457.1195.

***N*-Benzyl-*N*-(6-methyl-3-phenyl-1*H*-indol-2-yl)methanesulfonamide (4ja) & *N*-Benzyl-*N*-(4-methyl-3-phenyl-1*H*-indol-2-yl)methanesulfonamide (4ja′)**

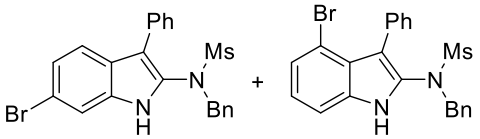


4ja **4ja'**

Inseparable mixture of **4ka** and **4ka′** (66% (48.5 mg), **4ka**:**4ka′** = 2.5:1) was obtained as a xx solid (EtOAc : *n*-Hexane = 1:4).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.20 (br s, 1H of **4ja′**), 8.12 (br s, 1H of **4ja**), 7.51-7.44 (m, 4H of **4ja** & 5H of **4ja′**), 7.41-7.36 (m, 2H of **4ja**), 7.29-7.17 (m, 5H of **4ja** & 5H of **4ja′**), 7.10 (d, J = 4.4 Hz, 2H of **4ja′**), 7.04 (s, 1H of **4ja**), 6.96 (d, J = 8.4 Hz, 1H of **4ja**), 6.82 (t, J = 3.8 Hz, 1H of **4ja′**), 4.73 (s, 2H of **4ja**), 4.60 (s, 2H of **4ja′**), 2.83 (s, 3H of **4ja**), 2.79 (s, 3H of **4ja′**), 2.44 (s, 3H of **4ja**), 2.06 (s, 3H of **4ja′**). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 136.32, 136.29, 135.1, 133.9, 133.6, 133.4, 131.4, 131.2, 129.2, 128.84, 128.79, 128.6, 128.5, 128.14, 128.06, 127.6, 127.4, 127.1, 125.2, 124.1, 123.1, 122.2, 121.6, 119.4, 113.4, 111.1, 109.1, 55.0, 40.1, 39.9, 21.7, 20.1 (6 carbons are missing due to overlapping). HRMS (EI) $[M]^+$ *m/z* calcd for $C_{23}H_{22}N_2O_2S$ 390.1397, found 390.1403.

***N*-Benzyl-*N*-(6-bromo-3-phenyl-1*H*-indol-2-yl)methanesulfonamide (4ka) & *N*-Benzyl-*N*-(4-bromo-3-phenyl-1*H*-indol-2-yl)methanesulfonamide (4ka′)**

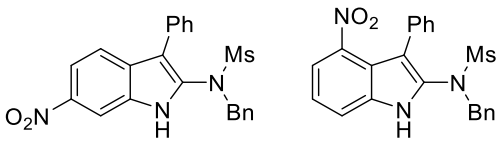


4ka **4ka'**

Inseparable mixture of **4ka** and **4ka′** (54% (30.8 mg), **4ka**:**4ka′** = 1.7:1) was obtained as a yellow oil (EtOAc : *n*-Hexane = 1:4).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.26 (br s, 1H of **4ka′**), 8.20 (br s, 1H of **4ka**), 7.52-7.39 (m, 5H of **4ka** & 7H of **4ka′**), 7.37 (d, J = 1.6 Hz, 1H of **4ka**), 7.29-7.17 (m, 7H of **4ka** & 5H of **4ka′**), 7.02 (t, J = 7.8 Hz, 1H of **4ka′**), 4.69 (s, 2H of **4ka**), 4.58 (s, 2H of **4ka′**), 2.85 (s, 3H of **4ka**), 2.79 (s, 3H of **4ka′**). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 136.1, 136.0, 134.2, 134.1, 133.2, 132.9, 131.9, 130.1, 129.3, 129.1, 128.79, 128.77, 128.6, 128.5, 128.4, 128.3, 127.93, 127.88, 127.6, 125.2, 125.0, 123.9, 123.8, 121.1, 116.9, 114.7, 114.4, 114.1, 113.8, 110.6, 55.1, 55.0, 40.4, 40.1 (2 carbons are missing due to overlapping). HRMS (EI) $[M+Na]^+$ *m/z* calcd for $C_{22}H_{19}BrN_2NaO_2S$ 477.0243, found 477.0246.

***N*-Benzyl-*N*-(6-nitro-3-phenyl-1*H*-indol-2-yl)methanesulfonamide (4la) & *N*-Benzyl-*N*-(4-nitro-3-phenyl-1*H*-indol-2-yl)methanesulfonamide (4la′)**



4la **4la'**

4la: 29% (13.5 mg), a yellow oil (EtOAc : *n*-Hexane = 1:4).

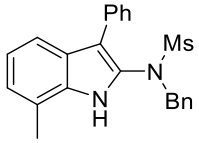
^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.96 (br s, 1H), 7.95 (s, 1H), 7.91 (dd, J = 9.0, 1.8 Hz, 1H), 7.59-7.55 (m,

3H), 7.50-7.46 (m, 3H), 7.30-7.28 (m, 3H), 7.22-7.19 (m, 2H), 4.75 (s, 2H), 2.92 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 143.9, 135.5, 133.0, 132.0, 131.6, 130.8, 129.4, 129.3, 128.9, 128.6, 128.5, 128.1, 119.6, 115.6, 114.2, 107.9, 54.8, 40.8. HRMS (EI) $[M+Na]^+$ *m/z* calcd for $C_{22}H_{19}N_3NaO_4S$ 444.0988, found 444.0991.

4la′: 28% (13.1 mg), a yellow solid (EtOAc : *n*-Hexane = 1:4), mp 198-200 °C.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.59 (br s, 1H), 7.74 (dd, J = 7.8, 0.6 Hz, 1H), 7.49-7.42 (m, 4H), 7.29-7.25 (m, 6H), 7.23-7.20 (m, 2H), 4.60 (s, 2H), 2.79 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 143.0, 135.8, 135.0, 133.4, 132.5, 129.3, 128.8, 128.6, 128.5, 128.4, 127.9, 122.0, 117.9, 117.6, 116.6, 113.1, 55.0, 40.4. HRMS (EI) $[M+Na]^+$ *m/z* calcd for $C_{22}H_{19}N_3NaO_4S$ 444.0988, found 444.0993.

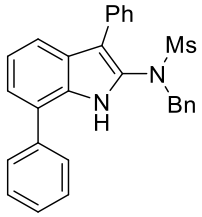
_N_-Benzyl-_N_-(7-methyl-3-phenyl-1_H_-indol-2-yl)methanesulfonamide (4ma)



66% (27.9 mg), a white solid (EtOAc : *n*-Hexane = 1:4), mp 142-144 °C.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.99 (br s, 1H), 7.51-7.43 (m, 5H), 7.41-7.37 (m, 1H), 7.29-7.23 (m, 5H), 7.07-7.03 (m, 2H), 4.75 (s, 2H), 2.81 (s, 3H), 2.33 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 136.4, 133.6, 133.1, 129.3, 128.88, 128.85, 128.7, 128.2, 127.9, 127.2, 125.9, 123.9, 120.6, 120.4, 117.4, 114.1, 55.1, 40.1, 16.4. HRMS (EI) $[M+Na]^+$ *m/z* calcd for $C_{23}H_{22}N_2NaO_2S$ 413.1294, found 413.1295.

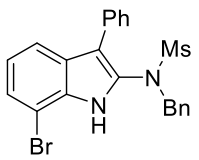
_N_-Benzyl-_N_-(3,7-diphenyl-1_H_-indol-2-yl)methanesulfonamide (4na)



69% (32.3 mg), a white solid (EtOAc : *n*-Hexane = 1:3), mp 155-157 °C.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.08 (br s, 1H), 7.63 (d, J = 7.6 Hz, 1H), 7.55-7.52 (m, 4H), 7.46-7.41 (m, 4H), 7.39-7.33 (m, 7H), 7.28 (d, J = 6.8 Hz, 1H), 7.23 (t, J = 7.6 Hz, 1H), 4.84 (s, 2H), 2.70 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 138.2, 136.7, 133.5, 131.2, 129.3, 129.1, 129.0, 128.93, 128.90, 128.3, 128.2, 127.8, 127.5, 127.3, 126.6, 125.5, 123.2, 121.0, 119.0, 114.4, 55.7, 40.3. HRMS (EI) $[M+Na]^+$ *m/z* calcd for $C_{28}H_{24}N_2NaO_2S$ 475.1451, found 475.1453.

_N_-Benzyl-_N_-(7-bromo-3-phenyl-1_H_-indol-2-yl)methanesulfonamide (4oa)

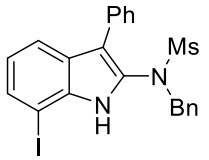


62% (59.4 mg), a yellow solid (EtOAc : *n*-Hexane = 1:5), mp 135-137 °C.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.23 (br s, 1H), 7.51 (t, J = 7.4 Hz, 2H), 7.48 (d, J = 7.2 Hz, 1H), 7.42 (d, J = 7.2 Hz, 3H), 7.37 (d, J = 7.6 Hz, 1H), 7.30-7.29 (m, 3H), 7.23-7.22 (m, 2H), 6.99 (t, J = 7.8 Hz, 1H), 4.74 (s, 2H), 2.82 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 135.9, 132.9, 132.3, 129.3, 129.0, 128.78, 128.75, 128.4, 127.6, 127.3, 125.8, 121.5, 118.9, 114.9, 104.6, 55.0, 40.4 (1 carbon is missing due to overlapping).

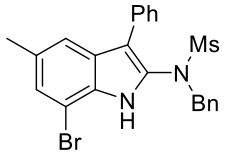
HRMS (EI) $[M+Na]^+$ *m/z* calcd for $C_{22}H_{19}BrN_2NaO_2S$ 477.0243, found 477.0242.

_N_-Benzyl-_N_-(7-iodo-3-phenyl-1_H_-indol-2-yl)methanesulfonamide (4pa)



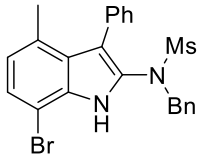
61% (35.1 mg), a yellow solid (EtOAc : *n*-Hexane = 1:5), mp 130-132 °C.
^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.07 (br s, 1H), 7.58 (dd, J = 7.6, 0.8 Hz, 1H), 7.54 (d, J = 8.0 Hz, 1H), 7.51-7.47 (m, 2H), 7.43-7.41 (m, 3H), 7.32-7.30 (m, 3H), 7.26-7.23 (m, 2H), 6.88 (t, J = 7.8 Hz, 1H), 4.76 (s, 2H), 2.80 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 136.0, 135.5, 133.1, 132.1, 129.3, 129.2, 129.0, 128.9, 128.8, 128.5, 128.4, 127.6, 126.2, 122.0, 119.8, 115.2, 55.1, 40.4. HRMS (EI) $[M]^+$ *m/z* calcd for $C_{22}H_{19}IN_2O_2S$ 502.0206, found 502.0208.

_N_-Benzyl-_N_-(7-bromo-5-methyl-3-phenyl-1_H_-indol-2-yl)methanesulfonamide (4qa)



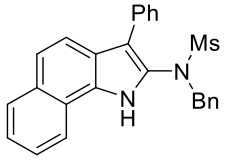
65% (34.3 mg), a yellow solid (EtOAc : *n*-Hexane = 1:5), mp 210-212 °C.
^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.10 (br s, 1H), 7.48 (t, J = 7.6 Hz, 2H), 7.41-7.38 (m, 3H), 7.29-7.28 (m, 4H), 7.22-7.20 (m, 3H), 4.72 (s, 2H), 2.81 (s, 3H), 2.37 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 136.0, 133.1, 131.3, 130.6, 129.3, 128.9, 128.79, 128.75, 128.3, 127.5, 127.4, 127.1, 118.5, 114.4, 104.2, 55.0, 40.3, 21.2 (1 carbon is missing due to overlapping). HRMS (EI) $[M+Na]^+$ *m/z* calcd for $C_{23}H_{21}BrN_2NaO_2S$ 491.0399, found 491.0402.

_N_-Benzyl-_N_-(7-bromo-4-methyl-3-phenyl-1_H_-indol-2-yl)methanesulfonamide (4ra)



67% (34.9 mg), a white solid (EtOAc : *n*-Hexane = 1:3), mp 180-182 °C.
^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.15 (br s, 1H), 7.45-7.41 (m, 3H), 7.33-7.29 (m, 5H), 7.26-7.22 (m, 3H), 6.69 (dd, J = 7.8, 0.6 Hz, 1H), 4.61 (s, 2H), 2.72 (s, 3H), 1.99 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 136.0, 134.4, 131.9, 131.1, 130.9, 129.2, 128.8, 128.6, 128.3, 128.2, 127.9, 125.9, 125.3, 122.8, 116.1, 102.0, 55.2, 40.1, 19.7. HRMS (EI) $[M]^+$ *m/z* calcd for $C_{23}H_{21}BrN_2O_2S$ 468.0502, found 468.0504.

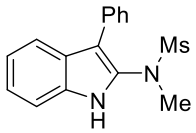
_N_-Benzyl-_N_-(3-phenyl-1_H_-benzo[_g_]indol-2-yl)methanesulfonamide (4sa)



68% (30.3 mg), a white solid (EtOAc : *n*-Hexane = 1:3), mp 203-205 °C.

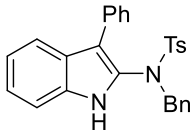
^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.78 (br s, 1H), 7.87 (d, J = 7.6 Hz, 1H), 7.79 (d, J = 8.0 Hz, 1H), 7.63 (d, J = 8.8 Hz, 1H), 7.54-7.41 (m, 8H), 7.30-7.28 (m, 5H), 4.79 (s, 2H), 2.83 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 136.4, 133.5, 130.9, 129.4, 129.0, 128.8, 128.7, 128.4, 128.3, 127.4, 126.1, 125.7, 124.6, 121.9, 121.3, 121.1, 119.8, 119.2, 115.6, 55.4, 40.1 (1 carbon is missing due to overlapping). HRMS (EI) $[M+Na]^+$ *m/z* calcd for $C_{26}H_{22}N_2NaO_2S$ 449.1294, found 449.1293.

_N_-Methyl-_N_-(3-phenyl-1_H_-indol-2-yl)methanesulfonamide (4ab)



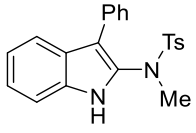
33% (10.2 mg) from **3ab**, a white solid (EtOAc : *n*-Hexane = 1:4), mp 162-164 °C.
^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.61 (br s, 1H), 7.61 (d, J = 8.0 Hz, 1H), 7.53-7.46 (m, 4H), 7.40-7.36 (m, 2H), 7.28 (td, J = 7.0, 1.0 Hz, 1H), 7.15 (td, J = 7.5, 1.0 Hz, 1H), 3.30 (s, 3H), 2.75 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 133.5, 133.4, 130.2, 129.4, 128.8, 127.2, 126.6, 123.6, 120.6, 119.7, 112.8, 111.3, 39.0, 38.5. LCMS *m*/*z* 301 $[M+H]^+$.
Spectral data were consistent with data reported in the literature.[8]

_N_-Benzyl-4-methyl-_N_-(3-phenyl-1_H_-indol-2-yl)benzenesulfonamide (4ac)



69% (84.4 mg), a white solid (EtOAc : *n*-Hexane = 1:6), mp 193-195 °C.
^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.51 (br s, 1H), 7.64 (d, J = 8.4 Hz, 2H), 7.49 (d, J = 8.0 Hz, 1H), 7.30 (d, J = 8.0 Hz, 3H), 7.25-7.16 (m, 7H), 7.09-7.05 (m, 3H), 6.64 (d, J = 7.2 Hz, 2H), 4.53 (s, 2H), 2.46 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 144.2, 136.1, 135.6, 133.2, 133.1, 129.9, 129.1, 128.4, 128.3, 127.8, 127.5, 126.8, 126.5, 123.0, 120.0, 119.4, 112.5, 111.0, 53.5, 21.6 (2 carbons are missing due to overlapping). EIMS *m*/*z* 452 (M^+), 297, 252, 207, 91.
Spectral data were consistent with data reported in the literature.[8]

_N_,4-Dimethyl-_N_-(3-phenyl-1_H_-indol-2-yl)benzenesulfonamide (4ad)



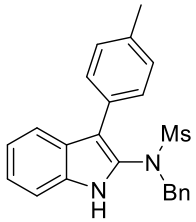
32% (12.1 mg) from **3ad**, a white solid (EtOAc : *n*-Hexane = 1:6), mp 180-182 °C.
^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.74 (br s, 1H), 7.58 (d, J = 8.0 Hz, 2H), 7.50 (d, J = 8.0 Hz, 1H), 7.39 (d, J = 8.0 Hz, 1H), 7.28-7.24 (m, 3H), 7.21 (t, J = 7.2 Hz, 1H), 7.15 (t, J = 7.6 Hz, 2H), 7.11 (t, J = 7.2 Hz, 1H), 6.67 (d, J = 7.6 Hz, 2H), 3.06 (s, 3H), 2.45 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 144.2, 134.1, 133.1, 133.0, 130.4, 129.8, 129.3, 128.1, 127.6, 126.67, 126.65, 123.0, 120.2, 119.4, 111.3, 110.9, 38.4, 21.6. LCMS *m*/*z* 377 $[M+H]^+$.

---

[8] Tian, X.; Song, L.; Rudolph, M.; Rominger, F.; Oeser, T.; Hashmi, A. S. K. *Angew. Chem., Int. Ed.* **2019**, *58*, 3589.

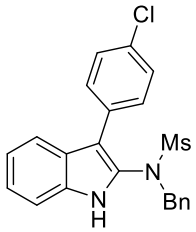
Spectral data were consistent with data reported in the literature.[8]

_N_-Benzyl-_N_-(3-(_p_-tolyl)-1_H_-indol-2-yl)methanesulfonamide (4af)



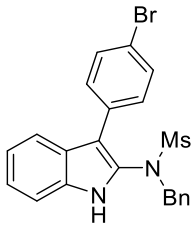
72% (30.8 mg), a beige solid (EtOAc : _n_-Hexane = 1:3), mp 192-194 °C.
^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.24 (br s, 1H), 7.62 (d, J = 8.0 Hz, 1H), 7.39 (d, J = 8.0 Hz, 2H), 7.33 (d, J = 8.0 Hz, 2H), 7.30-7.23 (m, 7H), 7.14 (ddd, J = 8.0, 6.0, 2.0 Hz, 1H), 4.75 (s, 2H), 2.88 (s, 3H), 2.48 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 137.0, 136.4, 133.4, 130.3, 129.6, 129.1, 128.71, 128.65, 128.1, 128.0, 126.5, 123.3, 120.3, 119.8, 113.3, 111.2, 54.8, 40.1, 21.3. HRMS (EI) $[M+Na]^+$ _m/z_ calcd for $C_{23}H_{22}N_2NaO_2S$ 413.1294, found 413.1296.

_N_-Benzyl-_N_-(3-(4-chlorophenyl)-1_H_-indol-2-yl)methanesulfonamide (4ag)



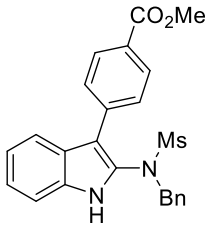
57% (25.5 mg), a white solid (EtOAc : _n_-Hexane = 1:2), mp 186-188 °C.
^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.30 (br s, 1H), 7.58 (d, J = 8.0 Hz, 1H), 7.47 (d, J = 8.4 Hz, 2H), 7.39 (d, J = 8.4 Hz, 2H), 7.29-7.24 (m, 5H), 7.22-7.19 (m, 2H), 7.16 (ddd, J = 8.0, 6.4, 1.6 Hz, 1H), 4.74 (s, 2H), 2.89 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 135.9, 133.5, 133.1, 131.8, 130.4, 129.1, 128.8, 128.7, 128.3, 128.2, 126.1, 123.6, 120.6, 119.5, 112.5, 111.3, 54.9, 40.3. HRMS (EI) $[M+Na]^+$ _m/z_ calcd for $C_{22}H_{19}ClN_2NaO_2S$ 433.0748, found 433.0750.

_N_-Benzyl-_N_-(3-(4-bromophenyl)-1_H_-indol-2-yl)methanesulfonamide (4ah)



65% (32.4 mg), a white solid (EtOAc : _n_-Hexane = 1:2), mp 188-190 °C.
^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.28 (br s, 1H), 7.59 (d, J = 7.2 Hz, 2H), 7.55 (d, J = 8.0 Hz, 1H), 7.30 (d, J = 7.2 Hz, 2H), 7.25-7.22 (m, 5H), 7.18-7.17 (m, 2H), 7.13 (t, J = 7.2 Hz, 1H), 4.71 (s, 2H), 2.87 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 135.9, 133.5, 132.3, 132.0, 130.7, 128.8, 128.7, 128.3, 128.2, 126.0, 123.6, 121.1, 120.7, 119.5, 112.6, 111.4, 54.9, 40.3. HRMS (EI) $[M+Na]^+$ _m/z_ calcd for $C_{22}H_{19}BrN_2NaO_2S$ 477.0243, found 477.0244.

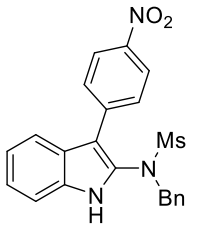
Methyl 4-(2-(*N*-Benzylmethylsulfonamido)-1*H*-indol-3-yl)benzoate (4ai)



71% (34.0 mg), a yellow oil (EtOAc : *n*-Hexane = 1:2).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.30 (br s, 1H), 8.15 (d, J = 8.0 Hz, 2H), 7.62 (d, J = 8.0 Hz, 1H), 7.53 (d, J = 8.4 Hz, 2H), 7.28-7.23 (m, 5H), 7.18-7.13 (m, 3H), 4.72 (s, 2H), 3.97 (s, 3H), 2.86 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 166.9, 138.4, 135.8, 133.6, 130.1, 128.9, 128.8, 128.7, 128.6, 128.3, 127.8, 125.8, 123.7, 120.8, 119.5, 112.7, 111.4, 54.9, 52.2, 40.3. HRMS (EI) $[M+Na]^+$ *m/z* calcd for $C_{24}H_{22}N_2NaO_4S$ 457.1192, found 457.1194.

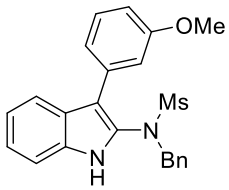
***N*-Benzyl-*N*-(3-(4-nitrophenyl)-1*H*-indol-2-yl)methanesulfonamide (4aj)**



46% (21.2 mg), a yellow solid (EtOAc : *n*-Hexane = 1:1), mp 186-188 °C.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.37 (br s, 1H), 8.31 (d, J = 8.8 Hz, 2H), 7.63 (d, J = 8.4 Hz, 1H), 7.60 (d, J = 8.8 Hz, 2H), 7.33-7.22 (m, 5H), 7.20 (ddd, J = 8.0, 6.0, 1.6 Hz, 1H), 7.14 (d, J = 6.4 Hz, 2H), 4.73 (s, 2H), 2.93 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 146.5, 140.5, 135.4, 133.6, 129.4, 129.1, 129.0, 128.8, 128.6, 125.4, 124.2, 124.1, 121.4, 119.4, 112.1, 111.6, 55.1, 40.5. HRMS (EI) $[M+Na]^+$ *m/z* calcd for $C_{22}H_{19}N_3NaO_4S$ 444.0988, found 444.0989.

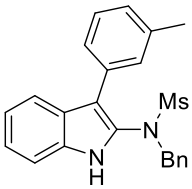
***N*-Benzyl-*N*-(3-(3-methoxyphenyl)-1*H*-indol-2-yl)methanesulfonamide (4ak)**



76% (44.3 mg), a yellow oil (EtOAc : *n*-Hexane = 1:3).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.28 (br s, 1H), 7.63 (d, J = 8.0 Hz, 1H), 7.41 (t, J = 8.2 Hz, 1H), 7.26-7.20 (m, 7H), 7.12 (ddd, J = 8.0, 6.4, 2.2 Hz, 1H), 7.07 (d, J = 7.6 Hz, 1H), 7.06 (d, J = 1.2 Hz, 1H), 6.95 (dd, J = 7.6, 2.0 Hz, 1H), 4.73 (s, 2H), 3.86 (s, 3H), 2.89 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 160.0, 136.3, 134.7, 133.4, 129.9, 128.69, 128.65, 128.2, 126.3, 123.4, 121.6, 120.4, 119.8, 115.0, 113.2, 112.6, 111.2, 55.3, 54.9, 40.2 (1 carbon is missing due to overlapping). HRMS (EI) $[M]^+$ *m/z* calcd for $C_{23}H_{22}N_2O_3S$ 406.1346, found 406.1353.

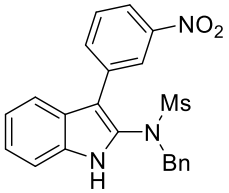
***N*-Benzyl-*N*-(3-(*m*-tolyl)-1*H*-indol-2-yl)methanesulfonamide (4al)**



66% (28.3 mg), a yellow solid (EtOAc : *n*-Hexane = 1:3), mp 162-164 °C.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.18 (br s, 1H), 7.60 (d, J = 8.0 Hz, 1H), 7.38 (t, J = 7.6 Hz, 1H), 7.27-7.20 (m, 10H), 7.12 (ddd, J = 8.0, 6.0, 2.0 Hz, 1H), 4.72 (s, 2H), 2.85 (s, 3H), 2.42 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 138.4, 136.3, 133.5, 133.3, 130.0, 128.8, 128.73, 128.66, 128.2, 128.1, 128.0, 126.4, 126.3, 123.3, 120.3, 119.8, 113.6, 111.2, 54.8, 40.1, 21.6. HRMS (EI) $[M+Na]^+$ *m/z* calcd for $C_{23}H_{22}N_2NaO_2S$ 413.1294, found 413.1296.

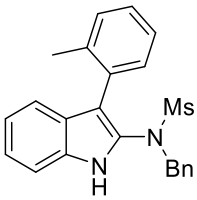
***N*-Benzyl-*N*-(3-(3-nitrophenyl)-1*H*-indol-2-yl)methanesulfonamide (4am)**



50% (23.2 mg), a yellow oil (EtOAc : *n*-Hexane = 1:1).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.69 (br s, 1H), 8.30 (s, 1H), 8.21 (dd, J = 8.4, 0.8 Hz, 1H), 7.80 (d, J = 7.6 Hz, 1H), 7.63 (t, J = 8.0 Hz, 1H), 7.62 (d, J = 8.8 Hz, 1H), 7.35 (d, J = 8.4 Hz, 1H), 7.30 (t, J = 6.4 Hz, 2H), 7.23-7.18 (m, 3H), 7.10 (d, J = 6.8 Hz, 2H), 4.71 (s, 2H), 3.05 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 148.5, 135.13, 135.05, 135.0, 133.6, 129.7, 128.8, 128.7, 128.6, 128.4, 125.4, 124.0, 123.6, 121.6, 121.1, 119.2, 111.6, 55.0, 40.3 (1 carbon is missing due to overlapping). HRMS (EI) $[M+Na]^+$ *m/z* calcd for $C_{22}H_{19}N_3NaO_4S$ 444.0988, found 444.0987.

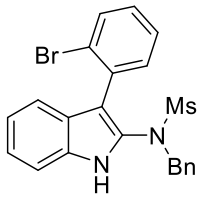
***N*-Benzyl-*N*-(3-(*o*-tolyl)-1*H*-indol-2-yl)methanesulfonamide (4an)**



68% (29.1 mg), a beige solid (EtOAc : *n*-Hexane = 1:3), mp 148-150 °C.

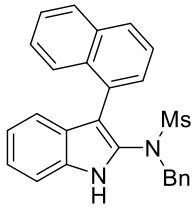
^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.23 (br s, 1H), 7.36-7.35 (m, 2H), 7.29-7.21 (m, 8H), 7.19 (d, J = 8.0 Hz, 2H), 7.06 (t, J = 7.8 Hz, 1H), 4.70 (d, J = 14.8 Hz, 1H), 4.53 (d, J = 15.2 Hz, 1H), 2.80 (s, 3H), 2.08 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 138.3, 136.4, 133.0, 132.5, 131.1, 130.6, 128.8, 128.7, 128.22, 128.19, 128.1, 126.9, 125.8, 123.1, 120.1, 120.0, 112.6, 111.2, 54.8, 40.0, 20.3. HRMS (EI) $[M+Na]^+$ *m/z* calcd for $C_{23}H_{22}N_2NaO_2S$ 413.1294, found 413.1295.

***N*-Benzyl-*N*-(3-(2-bromophenyl)-1*H*-indol-2-yl)methanesulfonamide (4ao)**



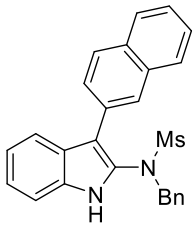
71% (38.7 mg), using 0.120 mmol of **1a** and **2o**; 62 % (307.7 mg), using 1.10 mmol of **1a** and **2o**.
a white solid (EtOAc : *n*-Hexane = 1:3), mp 114-116 °C.
^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.35 (br s, 1H), 7.77 (dd, J = 8.0, 1.2 Hz, 1H), 7.40 (td, J = 7.4, 1.6 Hz, 1H), 7.32 (td, J = 7.6, 2.0 Hz, 1H), 7.28-7.20 (m, 9H), 7.09 (td, J = 7.4, 1.2 Hz, 1H), 4.72 (d, J = 15.2 Hz, 1H), 4.66 (d, J = 14.8 Hz, 1H), 2.93 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 136.4, 134.4, 133.2, 133.0, 132.9, 129.6, 129.1, 128.7, 128.6, 128.1, 127.4, 126.7, 125.5, 123.3, 120.3, 120.2, 112.5, 111.2, 54.8, 40.5. HRMS (EI) $[M]^+$ *m/z* calcd for $C_{22}H_{19}BrN_2O_2S$ 454.0345, found 454.0355.

***N*-Benzyl-*N*-(3-(naphthalen-1-yl)-1*H*-indol-2-yl)methanesulfonamide (4ap)**



Two separable atropisomers (total 59%) was obtained.
Isomer **A**: 46% (21.3 mg), a white solid (EtOAc : *n*-Hexane = 1:6→1:3), mp 211-213 °C.
^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.44 (br s, 1H), 7.99 (d, J = 7.6 Hz, 2H), 7.64 (d, J = 8.4 Hz, 1H), 7.60 (t, J = 6.8 Hz, 1H), 7.55 (t, J = 7.6 Hz, 1H), 7.48 (d, J = 6.8 Hz, 1H), 7.39 (t, J = 7.6 Hz, 1H), 7.34 (d, J = 8.0 Hz, 1H), 7.29-7.25 (m, 4H), 7.17-7.16 (m, 2H), 7.12 (d, J = 8.0 Hz, 1H), 7.04 (t, J = 7.0 Hz, 1H), 4.68 (d, J = 14.8 Hz, 1H), 4.41 (d, J = 14.8 Hz, 1H), 2.78 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 136.2, 133.9, 133.1, 132.8, 130.8, 129.7, 128.6, 128.4, 128.0, 127.9, 126.5, 126.3, 126.2, 125.4, 123.2, 120.3, 120.2, 111.3, 111.1, 54.7, 40.0 (3 carbons are missing due to overlapping). HRMS (EI) $[M+Na]^+$ *m/z* calcd for $C_{26}H_{22}N_2NaO_2S$ 449.1294, found 449.1293.
Isomer **B**: 13% (6.1 mg), a yellow oil (EtOAc : *n*-Hexane = 1:6→1:3).
^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.05 (d, J = 8.0 Hz, 1H), 7.88 (d, J = 8.0 Hz, 1H), 7.71 (br s, 1H), 7.65 (td, J = 7.6, 1.2 Hz, 1H), 7.55 (d, J = 8.8 Hz, 1H), 7.49 (td, J = 7.6, 1.0 Hz, 2H), 7.40 (td, J = 7.4, 1.2 Hz, 1H), 7.26 (td, J = 7.4, 1.2 Hz, 2H), 7.16 (t, J = 7.6 Hz, 3H), 7.06 (d, J = 7.2 Hz, 2H), 6.99 (d, J = 8.8 Hz, 1H), 6.11 (br s, 1H), 4.75 (d, J = 13.6 Hz, 1H), 4.71 (d, J = 13.6 Hz, 1H), 3.16 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 135.3, 134.6, 131.9, 129.9, 128.8, 128.62, 128.55, 128.3, 128.1, 127.7, 126.4, 125.4, 124.2, 122.7, 116.8, 116.2, 112.2 , 54.4, 41.6 (5 carbons are missing due to overlapping). HRMS (EI) $[M+Na]^+$ *m/z* calcd for $C_{26}H_{22}N_2NaO_2S$ 449.1294, found 449.1296.

***N*-Benzyl-*N*-(3-(naphthalen-2-yl)-1*H*-indol-2-yl)methanesulfonamide (4aq)**



Two separable atropisomers (total 70%) was obtained.

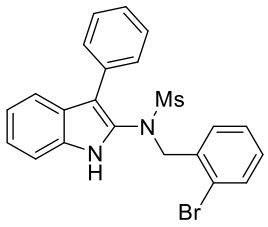
Isomer **A**: 51% (23.6 mg), a yellow solid (EtOAc : *n*-Hexane = 1:5→1:3), mp 190-192 °C.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.27 (br s 1H), 7.96 (d, J = 8.4 Hz, 1H), 7.92-7.90 (m, 1H), 7.88 (s, 1H), 7.86-7.83 (m, 1H), 7.66 (d, J = 8.0 Hz, 1H), 7.59 (dd, J = 8.4, 1.6 Hz, 1H), 7.55-7.53 (m, 2H), 7.29-7.19 (m, 7H), 7.14 (t, J = 7.8 Hz, 1H), 4.74 (s, 2H), 2.86 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 136.2, 133.63, 133.57, 132.4, 130.8, 128.8, 128.7, 128.5, 128.4, 128.2, 128.0, 127.9, 127.8, 127.3, 126.50, 126.45, 126.1, 123.5, 120.6, 119.8, 113.4, 111.3, 54.9, 40.2. HRMS (EI) $[M+Na]^+$ *m/z* calcd for $C_{26}H_{22}N_2NaO_2S$ 449.1294, found 449.1296.

Isomer **B**: 19% (8.9 mg), a yellow oil (EtOAc : *n*-Hexane = 1:5→1:3).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.86 (d, J = 8.0 Hz, 1H), 7.78 (dt, J = 8.0, 1.6 Hz, 1H), 7.73 (d, J = 8.8 Hz, 1H), 7.62 (d, J = 8.4 Hz, 1H), 7.57 (td, J = 7.6, 1.6 Hz, 1H), 7.49 (t, J = 7.4 Hz, 1H), 7.33 (td, J = 7.6, 1.2 Hz, 1H), 7.26 (tt, J = 7.4, 1.4 Hz, 2H), 7.17 (t, J = 8.0 Hz, 2H), 7.13 (td, J = 7.8, 1.4 Hz, 1H), 7.10-7.06 (m, 3H), 6.79 (d, J = 8.4 Hz, 1H), 6.13 (d, J = 8.0 Hz, 1H), 4.68 (s, 2H), 3.07 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 137.8, 134.6, 132.3, 130.7, 130.0, 129.2, 129.12, 129.10, 129.0, 128.9, 128.8, 128.6, 128.3, 125.5, 124.5, 122.7, 122.1, 121.2, 120.8, 117.3, 105.6, 54.7, 41.3 (1 carbon is missing due to overlapping). HRMS (EI) $[M+Na]^+$ *m/z* calcd for $C_{26}H_{22}N_2NaO_2S$ 449.1294, found 449.1286.

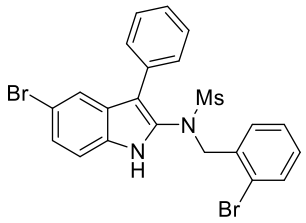
***N*-(2-Bromobenzyl)-*N*-(3-phenyl-1*H*-indol-2-yl)methanesulfonamide (4ar)**



58% (75.2 mg), a white solid (EtOAc : *n*-Hexane = 1:3), mp 97-99 °C.

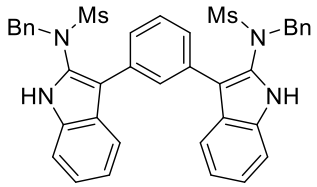
^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.39 (br s, 1H), 7.57 (d, J = 8.0 Hz, 1H), 7.48-7.36 (m, 7H), 7.31 (d, J = 8.0 Hz, 1H), 7.22 (t, J = 8.0 Hz, 2H), 7.14-7.08 (m, 2H), 4.94 (s, 2H), 2.90 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 135.2, 133.6, 133.1, 132.9, 130.5, 129.6, 129.4, 128.8, 127.81, 127.76, 127.3, 126.5, 123.9, 123.5, 120.5, 119.9, 114.2, 111.2, 54.5, 40.0. HRMS (EI) $[M+Na]^+$ *m/z* calcd for $C_{22}H_{19}BrN_2NaO_2S$ 477.0243, found 477.0245.

***N*-(5-Bromo-3-phenyl-1*H*-indol-2-yl)-*N*-(2-bromobenzyl)methanesulfonamide (4fr)**



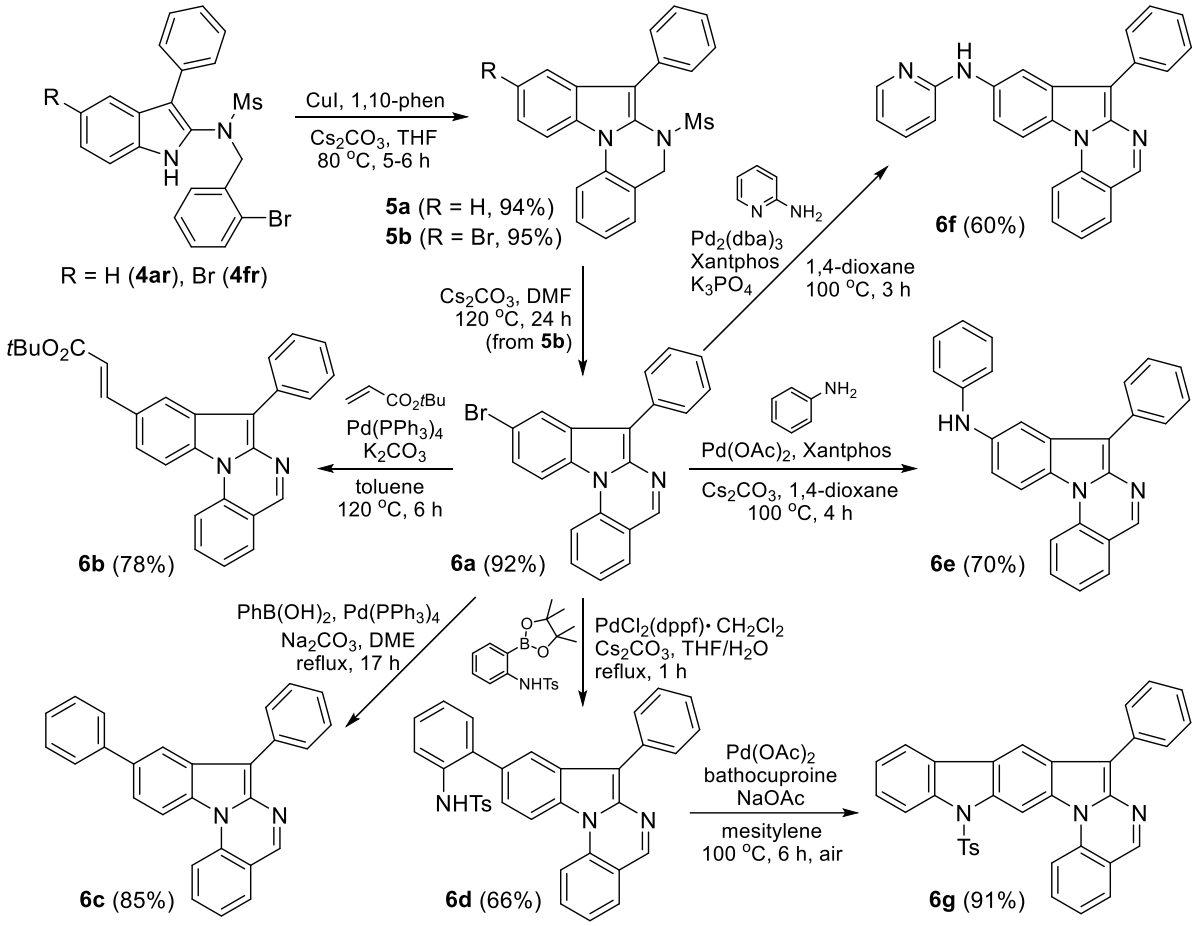
85% (762.8 mg), using 1.69 mmol of **1f** and **2r**, a white solid (EtOAc : *n*-Hexane = 1:3), mp 222-224 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.46 (br s, 1H), 7.66 (s, 1H), 7.47 (t, J = 7.4 Hz, 2H), 7.45 (dd, J = 8.0, 1.2 Hz, 1H), 7.40 (d, J = 7.2 Hz, 1H), 7.35 (t, J = 6.8 Hz, 3H), 7.30 (dd, J = 8.6, 1.8 Hz, 1H), 7.21 (t, J = 7.4 Hz, 1H), 7.14 (d, J = 9.2 Hz, 1H), 7.11 (td, J = 7.6, 1.2 Hz, 1H), 4.90 (s, 2H), 2.89 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 135.0, 132.9, 132.4, 132.1, 130.7, 129.8, 129.3, 129.0, 128.7, 128.2, 127.8, 127.6, 126.5, 124.0, 122.4, 113.9, 113.8, 112.7, 54.5, 40.2. HRMS (EI) $[M+Na]^+$ *m/z* calcd for $C_{22}H_{18}Br_2N_2NaO_2S$ 554.9348, found 554.9350.

***N,N'*-(1,3-Phenylenebis(1*H*-indole-3,2-diyl))bis(*N*-benzylmethanesulfonamide) (4as)**

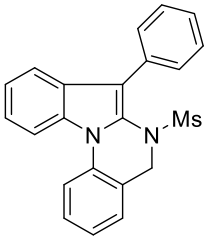


43% (25.5 mg), a white solid (EtOAc : *n*-Hexane = 1:2), mp 76-78 °C.
^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.29 (br s, 2H), 7.67-7.63 (m, 3H), 7.60 (d, J =7.4 Hz, 1H), 7.47 (dd, J = 7.4, 1.4 Hz, 2H), 7.28 (d, J = 8.0 Hz, 2H), 7.26-7.15 (m, 14H), 4.78 (s, 4H), 2.89 (s, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 136.1, 134.1, 133.5, 130.1, 129.5, 128.74, 128.73, 128.32, 128.30, 127.9, 126.2, 123.6, 120.7, 119.5, 113.0, 111.4, 54.9, 40.3. HRMS (EI) $[M]^+$ *m/z* calcd for $C_{38}H_{34}N_4O_4S_2$ 674.2016, found 674.2015.

Synthetic Application



6-(Methylsulfonyl)-7-phenyl-5,6-dihydroindolo[1,2-*a*]quinazoline (5a)



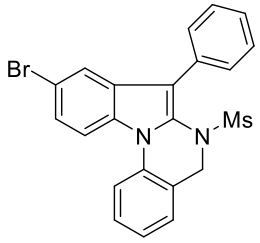
To a solution of **4ar** (48.6 mg, 0.107 mmol, 1 equiv) in THF (0.5 mL, 0.2 M) was added CuI (1.0 mg, 0.00534 mmol, 5 mol%), 1,10-phenanthroline (1.9 mg, 0.0107 mmol, 10 mol%), and Cs_2CO_3 (175.6 mg, 0.534 mmol, 5 equiv).[9] After being stirred at 80 °C for 5 h, the reaction mixture was cooled to rt. The resulting mixture was filtered through a pad of Celite. The filtrate was diluted with water and washed with CH_2Cl_2 (three times). The combined organic layer was washed with brine, dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by column chromatography on silica gel (EtOAc : *n*-Hexane = 1:3) to give **5a** (37.6 mg, 94%) as a bright yellow solid (mp 188-190 °C).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.01 (d, J = 8.4 Hz, 1H), 7.98 (d, J = 8.0 Hz, 1H), 7.82 (d, J = 8.0 Hz, 1H), 7.71 (d, J = 8.0 Hz, 2H), 7.53 (t, J = 8.0 Hz, 1H), 7.51 (t, J = 7.8 Hz, 2H), 7.45-7.34 (m, 3H), 7.30 (d, J = 7.6 Hz, 1H), 7.24 (t, J = 7.6 Hz, 1H), 4.91 (s, 2H), 2.32 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 135.2,

[9] Kiruthika, S. E.; Perumal, P. T. *Org. Lett.* **2014**, *16*, 484.

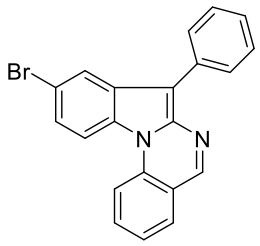
133.1, 131.9, 129.4, 129.3, 128.7, 128.6, 127.6, 127.10, 127.08, 125.4, 124.4, 124.1, 122.1, 120.6, 117.4, 112.6, 111.5, 49.2, 39.8. HRMS (EI) $[M+Na]^+$ *m/z* calcd for $C_{22}H_{18}N_2NaO_2S$ 397.0981, found 397.0984.

9-Bromo-6-(methylsulfonyl)-7-phenyl-5,6-dihydroindolo[1,2-*a*]quinazoline (5b)



95% (145.3 mg), using **4fr** (202.4 mg, 0.379 mmol) for 6 h.
a bright yellow solid (EtOAc : *n*-Hexane = 1:4), mp 202-204 °C.
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.93 (s, 1H), 7.91 (d, J = 9.2 Hz, 1H), 7.88 (d, J = 9.2 Hz, 1H), 7.68 (d, J = 7.2 Hz, 2H), 7.56-7.46 (m, 5H), 7.41 (t, J = 7.4 Hz, 1H), 7.28 (t, J = 7.4 Hz, 1H), 4.92 (s, 2H), 2.36 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 134.8, 132.4, 130.5, 129.63, 129.55, 129.3, 129.2, 128.9, 127.4, 127.2, 126.8, 125.5, 124.8, 123.0, 117.4, 115.3, 113.0, 112.1, 49.1, 40.1. HRMS (EI) $[M+Na]^+$ *m/z* calcd for $C_{22}H_{17}BrN_2NaO_2S$ 475.0086, found 475.0088.

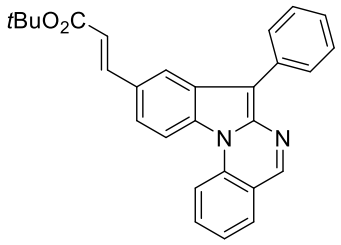
9-Bromo-7-phenylindolo[1,2-*a*]quinazoline (6a)



To a solution of **5b** (612.6 mg, 1.35 mmol, 1 equiv) in DMF (6.8 mL, 0.2 M) was added Cs_2CO_3 (533.6 mg, 1.62 mmol, 1.2 equiv).[10] After being stirred at 120 °C for 24 h, the reaction mixture was poured into water and then the product was extracted with EtOAc (three times). The combined organic layer was washed with brine, dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by column chromatography on silica gel (EtOAc : *n*-Hexane = 1:3) to give **6a** (463.0 mg, 92%) as a bright yellow solid (mp 216-218 °C).
^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.64 (s, 1H), 8.36 (d, J = 8.8 Hz, 1H), 8.24 (s, 1H), 8.23 (d, J = 9.6 Hz, 1H), 7.84-7.79 (m, 4H), 7.56 (t, J = 7.8 Hz, 3H), 7.42 (t, J = 7.4 Hz, 1H), 7.39 (t, J = 7.4 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 152.1, 139.5, 137.7, 133.7, 132.9, 129.94, 129.86, 129.4, 128.7, 128.2, 126.8, 125.8, 123.7, 122.9, 119.2, 116.1, 115.4, 114.6, 109.3. HRMS (EI) $[M+H]^+$ *m/z* calcd for $C_{21}H_{14}BrN_2$ 373.0335, found 373.0338.

[10] Han, W.; Zhou, X.; Yang, S.; Xiang, G.; Cui, B.; Chen, Y. *J. Org. Chem.* **2015**, *80*, 11580.

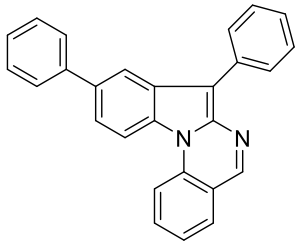
***tert*-Butyl (*E*)-3-(7-Phenylindolo[1,2-*a*]quinazolin-9-yl)acrylate (6b)**



To a solution of **6a** (12.8 mg, 0.0343 mmol, 1 equiv) in toluene (0.7 mL, 0.05 M) were added $Pd(PPh_3)_4$ (4.0 mg, 0.00343 mmol, 10 mol%), K_2CO_3 (14.2 mg, 0.103 mmol, 3 equiv), and *tert*-butyl acrylate (6.0 μL, 0.0377 mmol, 1.1 equiv). After being stirred at 120 °C for 6 h under Ar, the reaction mixture was cooled to room temperature and poured into water. Then the product was extracted with CH_2Cl_2 (three times). The combined organic layer was washed with brine, dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (EtOAc : *n*-Hexane = 1:6) to give **6b** (11.2 mg, 78%) as an orange solid (mp 225-227 °C).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.62 (s, 1H), 8.41 (d, J = 8.4 Hz, 1H), 8.34 (d, J = 8.8 Hz, 1H), 8.24 (s, 1H), 7.86 (d, J = 8.0 Hz, 2H), 7.83-7.76 (m, 3H), 7.67 (d, J = 8.8 Hz, 1H), 7.57 (t, J = 7.0 Hz, 2H), 7.42 (t, J = 6.8 Hz, 1H), 7.40 (t, J = 6.8 Hz, 1H), 6.45 (d, J = 16.0 Hz, 1H), 1.57 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 166.5, 151.7, 144.2, 139.4, 137.7, 133.6, 133.1, 130.1, 130.0, 129.3, 129.1, 128.7, 128.4, 126.8, 123.7, 122.3, 121.2, 119.2, 114.7, 114.4, 110.3, 80.4, 28.3 (1 carbon is missing due to overlapping). HRMS (EI) $[M+H]^+$ *m/z* calcd for $C_{28}H_{25}N_2O_2$ 421.1911, found 421.1911.

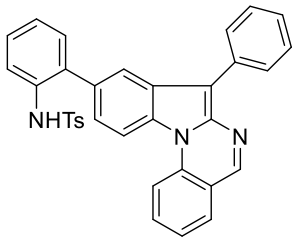
7,9-Diphenylindolo[1,2-*a*]quinazoline (6c)



6a (29.9 mg, 0.0801 mmol, 1 equiv), $PhB(OH)_2$ (14.7 mg, 0.120 mmol, 1.5 equiv), $Pd(PPh_3)_4$ (4.6 mg, 0.00401 mmol, 5 mol%), and 10% aq. Na_2CO_3 (80 μL, 1.0 M) were dissolved in DME (0.4 mL, 0.2 M). After being stirred at reflux for 17 h under Ar, the reaction mixture was cooled to room temperature and poured into water. Then the product was extracted with CH_2Cl_2 (three times), dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (EtOAc : *n*-Hexane = 1:3) to give **6c** (25.1 mg, 85%) as an orange solid (mp 230-232 °C).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.63 (s, 1H), 8.46 (d, J = 8.4 Hz, 1H), 8.43 (d, J = 8.8 Hz, 1H), 8.35 (s, 1H), 7.92 (d, J = 7.6 Hz, 2H), 7.83-7.76 (m, 3H), 7.73 (d, J = 8.0 Hz, 2H), 7.57 (t, J = 7.0 Hz, 2H), 7.49 (t, J = 7.0 Hz, 2H), 7.42-7.36 (m, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 151.4, 141.6, 139.3, 138.0, 135.8, 133.51, 133.50, 130.1, 129.2, 129.0, 128.8, 128.7, 127.6, 127.0, 126.6, 123.3, 122.8, 119.2, 118.7, 114.6, 114.3, 110.1 (1 carbon is missing due to overlapping). HRMS (EI) $[M+H]^+$ *m/z* calcd for $C_{27}H_{19}N_2$ 371.1543, found 371.1546.

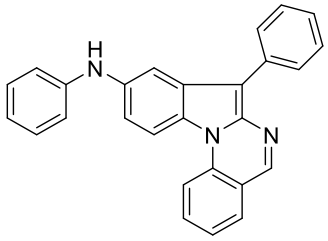
4-Methyl-*N*-(2-(7-phenylindolo[1,2-*a*]quinazolin-9-yl)phenyl)benzenesulfonamide (6d)



To a solution of **6a** (60.1 mg, 0.161 mmol, 1.0 equiv) in THF/H_2O (1:1, 3.2 mL, 0.05 M) were added $PdCl_2(dppf)\cdot CH_2Cl_2$ (13.1 mg, 0.0161 mmol, 10 mol%), Cs_2CO_3 (74.2 mg, 0.225 mmol, 1.4 equiv), and *N*-Ts-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (78.1 mg, 0.209 mmol, 1.3 equiv) under Ar.[11] After being stirred at reflux 90 °C for 1 h, the reaction mixture was poured into water and then the product was extracted with CH_2Cl_2 (three times). The combined organic layer was washed with brine, dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by column chromatography on silica gel (EtOAc : *n*-Hexane = 1:3) to give **6d** (57.7 mg, 66%) as an orange solid (mp 138-140 °C).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.68 (s, 1H), 8.47 (d, J = 8.0 Hz, 1H), 8.39 (d, J = 8.0 Hz, 1H), 7.88-7.82 (m, 4H), 7.73-7.70 (m, 2H), 7.53 (t, J = 7.4 Hz, 2H), 7.45 (t, J = 7.2 Hz, 1H), 7.42-7.39 (m, 3H), 7.34 (t, J = 8.4 Hz, 1H), 7.25 (d, J = 9.6 Hz, 1H), 7.16 (t, J = 7.8 Hz, 2H), 6.98 (d, J = 8.0 Hz, 2H), 6.82 (s, 1H), 2.24 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 152.1, 143.8, 139.7, 138.0, 136.0, 134.2, 134.1, 133.8, 133.2, 131.5, 130.7, 130.0, 129.5, 129.4, 129.1, 128.8, 128.7, 128.6, 127.2, 126.8, 124.6, 123.8, 123.5, 121.0, 120.6, 119.3, 114.7, 109.9, 21.4 (1 carbon is missing due to overlapping). HRMS (EI) $[M]^+$ *m/z* calcd for $C_{34}H_{25}N_3O_2S$ 539.1662, found 539.1664.

***N*,7-Diphenylindolo[1,2-*a*]quinazolin-9-amine (6e)**



To a solution of **6a** (191.1 mg, 0.512 mmol, 1.0 equiv) in 1,4-dioxane (1.0 mL, 0.5 M) were added $Pd(OAc)_2$ (5.9 mg, 0.0256 mmol, 5 mol%), Xantphos (15.5 mg, 0.0256 mmol, 5 mol%), Cs_2CO_3 (340.1 mg, 1.024 mmol, 2 equiv), and aniline (71 μL, 0.768 mmol, 1.5 equiv) under Ar.[12] After being stirred at 100 °C for 4 h, the reaction mixture was cooled to room temperature, filtered through a pad of Celite, and washed with EtOAc. The residue was concentrated in vacuo and purified by column chromatography on silica gel (EtOAc : *n*-Hexane = 1:3) to give **6e** (139.9 mg, 70%) as an orange solid (mp 198-200 °C).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.62 (s, 1H), 8.40 (d, J = 8.8 Hz, 1H), 8.30 (d, J = 8.8 Hz, 1H), 7.86 (dd, J = 8.0, 1.2 Hz, 1H), 7.84 (d, J = 2.0 Hz, 1H), 7.82-7.78 (m, 2H), 7.53 (t, J = 7.6 Hz, 2H), 7.38 (t, J = 7.6 Hz, 1H), 7.35 (t, J = 7.4 Hz, 2H), 7.27 (t, J = 7.8 Hz, 2H), 7.09 (d, J = 7.6 Hz, 2H), 6.90 (t, J = 7.2 Hz, 1H), 5.87 (br s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 151.1, 144.5, 139.5, 138.0, 137.9, 133.6, 133.5, 129.8, 129.5,

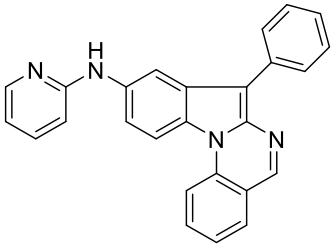
---

[11] Youn, S. W.; Ko, T. Y.; Jang, Y. H. *Angew. Chem., Int. Ed.* **2017**, *56*, 6636.

[12] Soussi, M. A.; Provot, O.; Bernadat, G.; Bignon, J.; Wdzieczak-Bakala, J.; Desravines, D.; Dubois, J.; Brion, J. -D. Messaoudi, S.; Alami, M. *Eur. J. Med. Chem.* **2014**, *78*, 178.

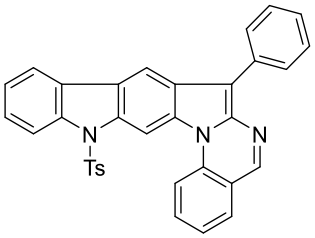
129.4, 129.2, 128.6, 126.4, 125.7, 123.0, 120.3, 119.0, 117.2, 116.4, 114.9, 114.4, 109.4, 109.2. HRMS (EI) $[M]^+$ *m/z* calcd for $C_{27}H_{19}N_3$ 385.1573, found 385.1573.

7-Phenyl-*N*-(pyridin-2-yl)indolo[1,2-*a*]quinazolin-9-amine (6f)



To a solution of **6a** (106.1 mg, 0.284 mmol, 1.0 equiv) in 1,4-dioxane (0.7 mL, 0.4 M) were added $Pd_2(dba)_3$ (10.1 mg, 0.0114 mmol, 4 mol%), Xantphos (20.3 mg, 0.0341 mmol, 12 mol%), K_3PO_4 (86.2 mg, 0.398 mmol, 1.4 equiv), and 2-aminopyridine (28.6 mg, 0.298 mmol, 1.05 equiv) under Ar.[13] After being stirred at 100 °C for 3 h, the reaction mixture was cooled to room temperature, filtered through a pad of Celite, and washed with EtOAc. The residue was concentrated in vacuo and purified by column chromatography on silica gel (EtOAc : *n*-Hexane = 1:2) to give **6f** (65.8 mg, 60%) as an orange solid (mp 202-204 °C).
^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.62 (s, 1H), 8.39 (d, J = 8.8 Hz, 1H), 8.32 (d, J = 8.8 Hz, 1H), 8.22 (d, J = 4.0 Hz, 1H), 8.05 (d, J = 2.0 Hz, 1H), 7.88 (d, J = 7.2 Hz, 2H), 7.81-7.77 (m, 2H), 7.54 (t, J = 7.8 Hz, 2H), 7.50-7.45 (m, 2H), 7.38 (t, J = 7.6 Hz, 1H), 7.36 (t, J = 7.6 Hz, 1H), 6.87 (d, J = 8.8 Hz, 1H), 6.86 (br s, 1H), 6.72 (dd, J = 7.0, 5.4 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 156.9, 151.3, 148.5, 139.5, 137.8, 137.7, 135.5, 133.5, 129.8, 129.2, 128.6, 126.5, 123.1, 119.0, 118.7, 114.8, 114.7, 114.4, 112.1, 109.4, 107.6 (3 carbons are missing due to overlapping). HRMS (EI) $[M]^+$ *m/z* calcd for $C_{26}H_{18}N_4$ 386.1526, found 386.1527.

7-Phenyl-13-tosyl-13*H*-quinazolino[1',2':1,5]pyrrolo[2,3-*b*]carbazole (6g)

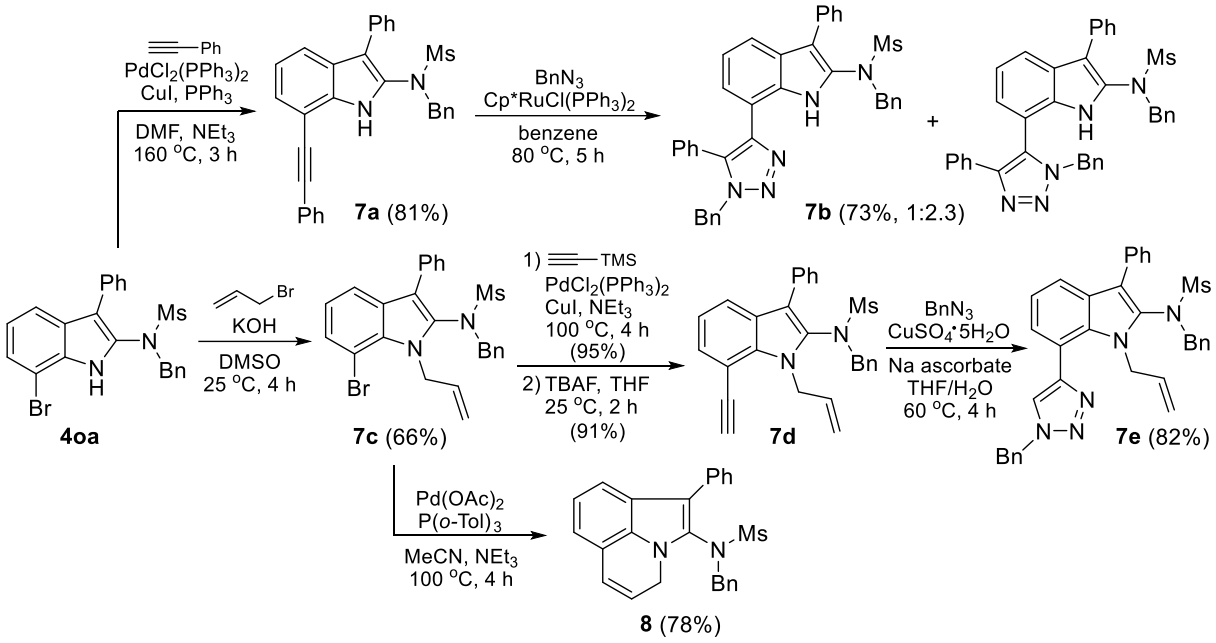


6d (30.7 mg, 0.0569 mmol, 1 equiv), $Pd(OAc)_2$ (1.3 mg, 0.00569 mmol, 10 mol%), bathocuproine (2.1 mg, 0.00569 mmol, 10 mol%), and NaOAc (4.8 mg, 0.0569 mmol, 1 equiv) were dissolved in mesitylene (0.6 mL, 0.1 M).[14] The resulting mixture was stirred at 100 °C in an oil bath under aerobic conditions. After 6 h, the reaction mixture was concentrated in vacuo. The residue was purified by column chromatography on silica gel (EtOAc : *n*-Hexane = 1:2) to give **6g** (27.8 mg, 91%) as a red solid (mp 271-273 °C).
^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.36 (s, 1H), 8.60 (d, J = 8.4 Hz, 1H), 8.57 (s, 1H), 8.48 (s, 1H), 8.31 (d, J = 8.0 Hz, 1H), 7.96-7.91 (m, 4H), 7.78 (dd, J = 7.6, 1.2 Hz, 1H), 7.67 (d, J = 8.4 Hz, 2H), 7.58 (t, J = 7.6 Hz, 2H), 7.48-7.39 (m, 3H), 7.36 (t, J = 7.2 Hz, 1H), 7.01 (d, J = 8.0 Hz, 2H), 2.19 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 151.5, 144.8, 139.6, 139.4, 137.9, 135.8, 134.5, 134.0, 133.4, 130.0, 129.6, 129.4,

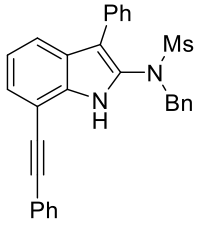
[13] Yin, J.; Zhao, M. M.; Huffman, M. A.; McNamara, J. M. *Org. Lett.* **2002**, *4*, 3481.

[14] Youn, S. W.; Kim, Y. H.; Jo, Y. H. *Adv. Synth. Catal.* **2019**, *361*, 462.

129.2, 128.7, 127.1, 126.9, 126.6, 126.4, 125.9, 124.2, 123.4, 123.3, 120.0, 119.2, 115.5, 114.5, 110.5, 109.5, 100.6, 21.4. HRMS (EI) $[M]^+$ *m/z* calcd for $C_{34}H_{23}N_3O_2S$ 537.1505, found 537.1511.



_N_-Benzyl-_N_-(3-phenyl-7-(phenylethynyl)-1_H_-indol-2-yl)methanesulfonamide (7a)

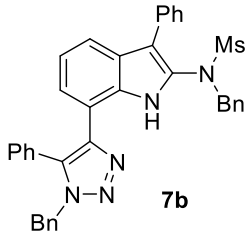


To a solution of **4oa** (59.4 mg, 0.130 mmol, 1.0 equiv) in DMF (0.5 mL, 0.25 M) and NEt_3 (0.3 mL, 0.5 M) were added $Pd(PPh_3)_2Cl_2$ (7.0 mg, 0.00978 mmol, 7.5 mol%), CuI (3.8 mg, 0.0196 mmol, 15 mol%), PPh_3 (16.2 mg, 0.0587 mmol, 45 mol%), and phenylacetylene (37 μL, 0.326 mmol, 2.5 equiv) under Ar.[15] After being stirred at 160 °C for 3 h, the reaction mixture was poured into water and then the product was extracted with EtOAc (three times). The combined organic layer was washed with brine, dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by column chromatography on silica gel (EtOAc : *n*-Hexane = 1:1) to give **7a** (50.1 mg, 81%) as a yellow solid (mp 163-165 °C).

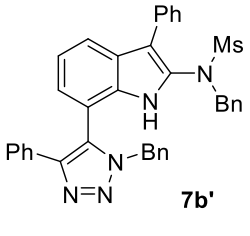
^1H NMR ($CDCl_3$, 400 MHz) δ 8.34 (br s, 1H), 7.60 (d, J = 8.0 Hz, 1H), 7.56-7.54 (m, 2H), 7.53-7.45 (m, 4H), 7.44-7.38 (m, 5H), 7.30-7.24 (m, 5H), 7.12 (t, J = 7.8 Hz, 1H), 4.80 (s, 2H), 2.79 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 136.3, 134.1, 133.1, 131.7, 129.3, 129.0, 128.9, 128.8, 128.5, 128.42, 128.35, 127.4, 126.6, 125.8, 122.9, 120.5, 120.4, 114.4, 106.4, 94.1, 84.7, 55.2, 40.4 (1 carbon is missing due to overlapping). HRMS (EI) $[M]^+$ *m/z* calcd for $C_{30}H_{24}N_2O_2S$ 476.1553, found 476.1557.

[15] Chen, S.; Wang, L.; Zhang, J.; Hao, Z.; Huang, H.; Deng, G.-J. *J. Org. Chem.* **2017**, *82*. 11182.

***N*-Benzyl-*N*-(7-(1-benzyl-5-phenyl-1*H*-1,2,3-triazol-4-yl)-3-phenyl-1*H*-indol-2-yl)methanesulfonamide (7b) & *N*-Benzyl-*N*-(7-(1-benzyl-4-phenyl-1*H*-1,2,3-triazol-5-yl)-3-phenyl-1*H*-indol-2-yl)methanesulfonamide (7b′)**



7b



7b'

To a solution of **7a** (46.8 mg, 0.0982 mmol, 1.0 equiv) in benzene (1.0 mL, 0.1 M) were added Cp*RuCl(PPh$_3$)$_2$ (0.8 mg, 0.000982 mmol, 1 mol%) and benzyl azide (20 μL, 0.147 mmol, 1.5 equiv).[16] After being stirred at 80 °C for 5 h, the reaction mixture was concentrated in vacuo. The residue was purified by column chromatography on silica gel (EtOAc : *n*-Hexane = 1:2) to give **7b** (total 43.7 mg, 73%, **A**:**B** = 1:2.3). Regiochemistry could not be determined and two regioisomers were obtained with a 1:2.3 (= **A** : **B**) ratio.

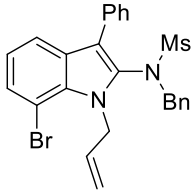
Isomer **A:** 22% (13.2 mg), a brown solid (EtOAc : *n*-Hexane = 1:2), mp 83-85 °C.

^{1}H NMR (CDCl$_3$, 400 MHz) δ 10.75 (br s, 1H), 7.54 (tt, J = 7.4, 1.4 Hz, 1H), 7.50-7.46 (m, 3H), 7.41 (d, J = 4.0 Hz, 4H), 7.37-7.31 (m, 1H), 7.29-7.26 (m, 8H), 7.21 (dd, J = 8.4, 1.6 Hz, 2H), 7.05-7.02 (m, 2H), 6.86 (dd, J = 7.6, 1.2 Hz, 1H), 6.82 (t, J = 7.6 Hz, 1H), 5.41 (s, 2H), 4.82 (s, 2H), 2.87 (s, 3H). ^{13}C NMR (CDCl$_3$, 100 MHz) δ 143.4, 135.8, 135.1, 133.8, 133.5, 131.3, 130.2, 130.0, 129.5, 129.4, 128.9, 128.74, 128.68, 128.6, 128.3, 128.1, 128.0, 127.6, 127.2, 126.9, 119.8, 119.64, 119.58, 114.2, 114.0, 55.3, 52.1, 40.7 (1 carbon is missing due to overlapping). HRMS (EI) [M]$^+$ *m/z* calcd for $C_{37}H_{31}N_5O_2S$ 609.2193, found 609.2206.

Isomer **B:** 51% (30.5 mg), a brown solid (EtOAc : *n*-Hexane = 1:2), mp 244-246 °C.

^{1}H NMR (CDCl$_3$, 400 MHz) δ 10.99 (br s, 1H), 7.74 (d, J = 8.0 Hz, 1H), 7.54-7.51 (m, 2H), 7.45-7.35 (m, 5H), 7.20-7.07 (m, 12H), 6.87 (dd, J = 7.2, 0.4 Hz, 1H), 6.81 (dd, J = 8.0, 1.6 Hz, 2H), 4.98 (d, J = 14.0 Hz, 1H), 4.88 (d, J = 14.8 Hz, 1H), 4.84 (d, J = 14.0 Hz, 1H), 4.75 (d, J = 13.6 Hz, 1H), 2.79 (s, 3H). ^{13}C NMR (CDCl$_3$, 100 MHz) δ 144.8, 135.3, 134.9, 132.9, 130.9, 130.2, 129.7, 129.6, 129.2, 128.63, 128.56, 128.5, 128.4, 128.2, 128.01, 127.98, 127.9, 127.5, 127.1, 126.4, 125.2, 122.1, 120.3, 116.2, 110.1, 54.5, 52.2, 40.5 (1 carbon is missing due to overlapping). HRMS (EI) [M]$^+$ *m/z* calcd for $C_{37}H_{31}N_5O_2S$ 609.2193, found 609.2204.

***N*-(1-Allyl-7-bromo-3-phenyl-1*H*-indol-2-yl)-*N*-benzylmethanesulfonamide (7c)**

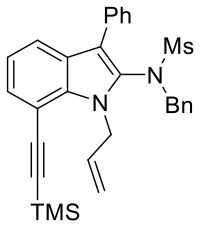


To a solution of **4oa** (159.9 mg, 0.351 mmol, 1.0 equiv) in DMSO (0.4 mL, 0.9 M) was added KOH (84.7 mg, 1.404 mmol, 4 equiv). After being stirred at 25 °C for 15 min, allyl bromide (62 μL, 0.702 mmol, 2

[16] Zhang, L.; Chen, X.; Xue, P.; Sun, H. H. Y.; Williams, I. D.; Sharpless, K. B.; Fokin, V. V.; Jia, G. *J. Am. Chem. Soc.* **2005**, *127*, 15998.

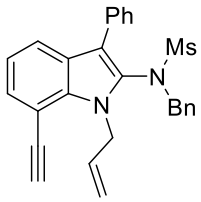
equiv) was added dropwise and stirring continued for a further 4 h.[17] The reaction mixture was poured into water and then the product was extracted with CH_2Cl_2 (three times). The combined organic layer was washed with brine, dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by column chromatography on silica gel (EtOAc : *n*-Hexane = 1:5) to give **7c** (114.5 mg, 66%) as a yellow oil.
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.43 (dd, J = 7.6, 1.2 Hz, 1H), 7.39-7.34 (m, 4H), 7.31-7.29 (m, 1H), 7.26-7.20 (m, 4H), 7.11 (dd, J = 8.0, 1.2 Hz, 2H), 6.92 (t, J = 7.6 Hz, 1H), 5.99-5.89 (m, 1H), 5.11 (d, J = 9.6 Hz, 1H), 5.10-5.03 (m, 1H), 4.95-4.86 (m, 2H), 4.74 (d, J = 14.4 Hz, 1H), 4.66 (d, J = 14.4 Hz, 1H), 2.57 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 135.4, 134.9, 132.8, 132.0, 131.3, 130.3, 129.8, 129.6, 128.9, 128.8, 128.6, 128.5, 127.6, 121.2, 119.5, 116.3, 116.0, 104.1, 56.3, 45.7, 41.4. HRMS (EI) $[M]^+$ *m/z* calcd for $C_{25}H_{23}BrN_2O_2S$ 494.0658, found 494.0665.

***N*-(1-Allyl-3-phenyl-7-((trimethylsilyl)ethynyl)-1*H*-indol-2-yl)-*N*-benzylmethanesulfonamide**



To a solution of **7c** (113.3 mg, 0.229 mmol, 1.0 equiv) in NEt_3 (5.7 mL, 0.04 M) were added $Pd(PPh_3)_2Cl_2$ (16.1 mg, 0.0229 mmol, 10 mol%), CuI (4.4 mg, 0.0229 mmol, 10 mol%), and trimethylsilylacetylene (65 μL, 0.457 mmol, 2.0 equiv) under Ar.[18] After being stirred at 100 °C for 4 h, the reaction mixture was concentrated in vacuo. The residue was purified by column chromatography on silica gel (EtOAc : *n*-Hexane = 1:5) to give the corresponding product (111.5 mg, 95%) as a yellow oil.
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.43 (dd, J = 7.6, 2.0 Hz, 2H), 7.35-7.29 (m, 4H), 7.26-7.22 (m, 2H), 7.20-7.16 (m, 2H), 7.11 (dd, J = 7.2, 1.2 Hz, 2H), 7.02 (t, J = 7.6 Hz, 1H), 6.07-5.97 (m, 1H), 5.22 (dq, J = 17.4, 1.5 Hz, 1H), 5.13 (dd, J = 10.6, 0.6 Hz, 1H), 5.01-4.94 (m, 2H), 4.82 (d, J = 14.4 Hz, 1H), 4.66 (d, J = 14.4 Hz, 1H), 2.56 (s, 3H), 0.27 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 135.5, 135.1, 133.13, 133.09, 131.1, 130.2, 130.1, 129.8, 128.7, 128.5, 128.4, 127.4, 127.3, 121.2, 119.8, 116.1, 115.9, 106.6, 103.1, 98.0, 56.3, 45.6, 41.4, -0.2. HRMS (EI) $[M]^+$ *m/z* calcd for $C_{30}H_{32}N_2O_2SSi$ 512.1948, found 512.1952.

***N*-(1-Allyl-7-ethynyl-3-phenyl-1*H*-indol-2-yl)-*N*-benzylmethanesulfonamide (7d)**



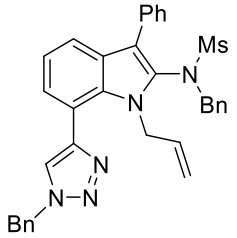
To a solution of the above TMS-alkynyl-substituted indole (67.6 mg, 0.132 mmol, 1.0 equiv) in THF (4.4 mL, 0.03 M) was added nBu$_4$NF (165 μL, 0.165 mmol, 1.25 equiv, 1.0 M solution in THF).[18] After being stirred at 25 °C for 2 h, the reaction mixture was quenched with sat. aq. NH_4Cl, extracted with EtOAc (three times), dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by column chromatography

[17] Black, D. S.; Keller, P. A.; Kumar, N. *Tetrahedron* **1992**, *48*, 7601.

[18] Kotha, S.; Aswar, V. R.; Singhal, G. *Tetrahedron* **2017**, *73*, 6436.

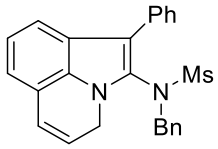
on silica gel (EtOAc : *n*-Hexane = 1:5) to give **7d** (53.2 mg, 91%) as a yellow oil.
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.48 (dd, J = 8.0, 0.8 Hz, 1H), 7.47 (dd, J = 7.6, 1.2 Hz, 1H), 7.38-7.29 (m, 4H), 7.27-7.25 (m, 2H), 7.24-7.20 (m, 2H), 7.12 (dd, J = 8.4, 1.6 Hz, 2H), 7.05 (t, J = 7.6 Hz, 1H), 6.04-5.94 (m, 1H), 5.16-5.10 (m, 2H), 5.02-4.92 (m, 2H), 4.79 (d, J = 14.4 Hz, 1H), 4.67 (d, J = 14.4 Hz, 1H), 3.27 (s, 1H), 2.59 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 135.3, 135.1, 133.2, 133.0, 131.2, 130.5, 130.2, 129.7, 128.7, 128.51, 128.46, 127.43, 127.36, 121.5, 119.9, 116.1, 116.0, 105.4, 81.9, 80.8, 56.3, 45.6, 41.4. HRMS (EI) $[M]^+$ *m/z* calcd for $C_{27}H_{24}N_2O_2S$ 440.1553, found 440.1558.

_N_-(1-Allyl-7-(1-benzyl-1_H_-1,2,3-triazol-4-yl)-3-phenyl-1_H_-indol-2-yl)-_N_-benzylmethanesulfonamide (7e)



To a solution of **7d** (20.2 mg, 0.0459 mmol, 1.0 equiv) in THF/H_2O (3:1, 1.1 mL, 0.04 M) were added $CuSO_4 \cdot 5H_2O$ (2.3 mg, 0.00917 mmol, 20 mol%), Na-ascorbate (8.3 mg, 0.0413 mmol, 0.9 equiv), and benzyl azide (6 μL, 0.0459 mmol, 1 equiv) under Ar.[19] After being stirred at 60 °C for 4 h, the reaction mixture was poured into water and then the product was extracted with EtOAc (three times). The combined organic layer was washed with brine, dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by column chromatography on silica gel (EtOAc : *n*-Hexane = 1:2) to give **7e** (21.5 mg, 82%) as a colorless oil.
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.52 (dd, J = 7.8, 1.4 Hz, 1H), 7.47 (s, 1H), 7.41-7.34 (m, 7H), 7.31-7.28 (m, 3H), 7.26-7.22 (m, 3H), 7.16-7.08 (m, 4H), 5.60 (d, J = 15.6 Hz, 1H), 5.57 (d, J = 14.8 Hz, 1H), 5.21-5.12 (m, 1H), 4.70 (d, J = 14.4 Hz, 1H), 4.65 (d, J = 14.4 Hz, 1H), 4.62-4.48 (m, 2H), 4.43 (dq, J = 10.6, 1.4 Hz, 1H), 4.22 (dq, J = 17.2, 1.2 Hz, 1H), 2.57 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 147.3, 135.0, 134.7, 134.6, 133.5, 132.1, 131.5, 130.3, 129.8, 129.1, 128.9, 128.8, 128.53, 128.49, 128.21, 128.18, 127.4, 127.2, 123.0, 120.8, 119.7, 115.9, 115.4, 114.9, 56.6, 54.3, 46.1, 41.3. HRMS (EI) $[M]^+$ *m/z* calcd for $C_{34}H_{31}N_5O_2S$ 573.2193, found 573.2189.

_N_-Benzyl-_N_-(1-phenyl-4_H_-pyrrolo[3,2,1-_ij_]quinolin-2-yl)methanesulfonamide (8)

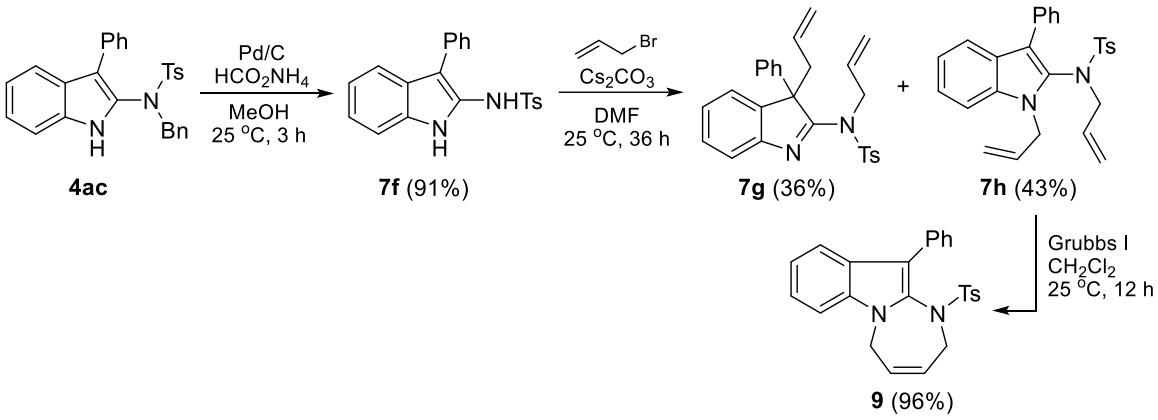


To a solution of **7c** (41.3 mg, 0.0834 mmol, 1.0 equiv) in MeCN/NEt_3 (10:1, 1.7 mL, 0.05 M) were added $Pd(OAc)_2$ (4.8 mg, 0.0208 mmol, 25 mol%) and P(*o*-Tol)$_3$ (10.7 mg, 0.0333 mmol, 40 mol%) under Ar.[17] After being stirred at 100 °C for 4 h, the reaction mixture was concentrated in vacuo. The residue was purified by column chromatography on silica gel (EtOAc : *n*-Hexane = 1:5) to give **8** (26.9 mg, 78%) as a brown solid (mp 150-152 °C).

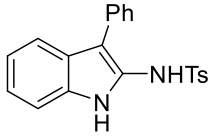
---

[19] Gee, H.-C.; Lee, C.-H.; Jeong, Y.-H.; Jang, W.-D. *Chem. Commun*. **2011**, *47*, 11963.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.49-7.44 (m, 4H), 7.39-7.28 (m, 7H), 6.93 (dd, J = 8.0, 7.2 Hz, 1H), 6.79 (d, J = 6.8 Hz, 1H), 6.46 (dt, J = 10.0, 2.2 Hz, 1H), 5.62 (dt, J = 10.0, 3.6 Hz, 1H), 5.01 (dt, J = 18.6, 2.7 Hz, 1H), 4.95 (d, J = 14.0 Hz, 1H), 4.59 (d, J = 14.0 Hz, 1H), 3.92 (dt, J = 18.6, 2.9 Hz, 1H), 2.61 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 135.8, 134.0, 131.6, 129.7, 129.5, 129.0, 128.8, 128.6, 127.2, 123.3, 123.2, 122.9, 120.9, 119.7, 119.4, 118.2, 115.1, 56.8, 44.6, 40.6 (1 carbon is missing due to overlapping). HRMS (EI) $[M]^+$ *m/z* calcd for $C_{25}H_{22}N_2O_2S$ 414.1397, found 414.1402.



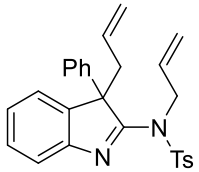
4-Methyl-*N*-(3-phenyl-1*H*-indol-2-yl)benzenesulfonamide (7f)



To a solution of **4ac** (138.1 mg, 0.305 mmol, 1.0 equiv) in MeOH (30.5 mL, 0.01 M) were added HCO_2NH_4 (192.4 mg, 3.05 mmol, 10 equiv) and 10% Pd/C (162.4 mg, 0.153 mmol, 0.5 equiv) under Ar. After being stirred at 25 °C for 3 h, the reaction mixture was filtered through Celite and concentrated in vacuo. The residue was purified by column chromatography on silica gel (EtOAc : *n*-Hexane = 1:5) to give **7f** (100.6 mg, 91%) as a white solid (mp 149-151 °C).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.01 (br s, 1H), 7.49 (d, J = 8.0 Hz, 2H), 7.40 (d, J = 8.0 Hz, 1H), 7.26-7.20 (m, 4H), 7.12-7.08 (m, 4H), 6.87 (dd, J = 8.0, 1.2 Hz, 2H), 2.34 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 144.4, 134.8, 133.1, 132.4, 129.7, 128.74, 128.65, 127.0, 126.8, 126.6, 126.2, 122.5, 120.4, 118.9, 111.1, 107.9, 21.5. LCMS *m/z* 364 $[M+2H]^+$. HRMS (EI) $[M]^+$ *m/z* calcd for $C_{21}H_{18}N_2O_2S$ 362.1083, found 362.1088.

***N*-Allyl-*N*-(3-allyl-3-phenyl-3*H*-indol-2-yl)-4-methylbenzenesulfonamide (7g)**

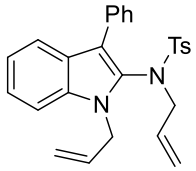


Allyl bromide (13 µl, 0.150 mmol, 2.2 equiv) was added dropwise to a solution of **7f** (24.7 mg, 0.0681

mmol, 1 equiv) and Cs_2CO_3 (67.2 mg, 0.204 mmol, 3.0 equiv) in DMF (0.1 mL, 0.5 M). After being stirred at 25 °C for 36 h, the reaction mixture was poured into water and then the product was extracted with EtOAc (three times). The combined organic layer was washed with brine, dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by column chromatography on silica gel (EtOAc : *n*-Hexane = 1:5 → 1:3) to give **7g** (10.7 mg, 36%) as a yellow oil and **7h** (13.1 mg, 43%) as a white solid (mp 131-133 °C).

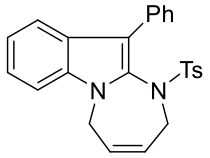
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.44 (d, J = 8.0 Hz, 2H), 7.25-7.21 (m, 4H), 7.15-7.13 (m, 2H), 7.11 (d, J = 8.0 Hz, 2H), 7.04 (t, J = 7.4 Hz, 1H), 6.95 (d, J = 7.6 Hz, 1H), 6.92 (d, J = 8.0 Hz, 1H), 5.88-5.78 (m, 1H), 5.35-5.27 (m, 2H), 5.24 (d, J = 10.4 Hz, 1H), 5.12 (dd, J = 16.0, 0.8 Hz, 1H), 4.93 (dd, J = 10.0, 1.6 Hz, 1H), 4.59 (dd, J = 15.8, 5.4 Hz, 1H), 4.51 (dd, J = 15.8, 5.8 Hz, 1H), 4.18 (dd, J = 13.0, 8.2 Hz, 1H), 3.14 (dd, J = 12.8, 6.4 Hz, 1H), 2.36 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 169.9, 141.8, 141.2, 140.5, 139.1, 136.9, 131.4, 130.6, 128.8, 128.5, 127.9, 127.3, 126.5, 126.3, 124.1, 123.4, 120.3, 118.6, 109.6, 60.1, 44.9, 39.7, 21.4. HRMS (EI) $[M]^+$ *m/z* calcd for $C_{27}H_{26}N_2O_2S$ 442.1710, found 442.1709.

_N_-Allyl-_N_-(1-allyl-3-phenyl-1_H_-indol-2-yl)-4-methylbenzenesulfonamide (7h)



^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.53 (d, J = 8.0 Hz, 1H), 7.47 (d, J = 6.8 Hz, 2H), 7.39 (d, J = 8.4 Hz, 1H), 7.30-7.26 (m, 1H), 7.24-7.16 (m, 3H), 7.14-7.07 (m, 5H), 6.09-6.00 (m, 1H), 5.85-5.75 (m, 1H), 5.29-5.23 (m, 2H), 5.07-5.02 (m, 2H), 4.95-4.84 (m, 2H), 4.43 (ddd, J = 14.2, 6.0, 1.0 Hz, 1H), 3.95 (dd, J = 14.2, 7.8 Hz, 1H), 2.40 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 143.6, 136.2, 134.6, 134.0, 133.4, 132.6, 129.6, 129.5, 129.4, 128.1, 127.7, 126.3, 123.0, 120.1, 119.8, 117.2, 115.0, 111.1, 55.5, 46.4, 21.5 (2 carbons are missing due to overlapping). HRMS (EI) $[M]^+$ *m/z* calcd for $C_{27}H_{26}N_2O_2S$ 442.1710, found 442.1714.

11-Phenyl-1-tosyl-2,5-dihydro-1_H_-[1,3]diazepino[1,2-_a_]indole (9)

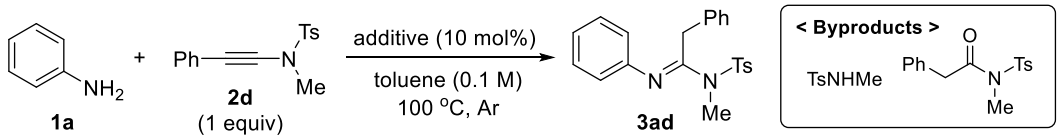


To a solution of **7h** (13.1 mg, 0.0296 mmol, 1 equiv) in CH_2Cl_2 (0.2 mL, 0.1 M) was added Grubbs 1st generation catalyst (1.2 mg, 0.00148 mmol, 5 mol%) under Ar. After being stirred at 25 °C for 12 h, the solvent was evaporated and the residue was purified by column chromatography on silica gel (EtOAc : *n*-Hexane = 1:5) to give **9** (11.8 mg, 96%) as a white solid (mp 89-91 °C).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.67 (d, J = 8.0 Hz, 1H), 7.34 (t, J = 7.4 Hz, 1H), 7.29 (t, J = 7.4 Hz, 1H), 7.28 (d, J = 8.0 Hz, 2H), 7.21-7.18 (m, 5H), 7.12 (t, J = 7.4 Hz, 1H), 6.85 (d, J = 8.0 Hz, 2H), 6.04-5.98 (m, 1H), 5.82 (dt, J = 11.6, 2.0 Hz, 1H), 5.02 (dt, J = 17.2, 3.0 Hz, 1H), 4.93 (d, J = 18.4 Hz, 1H), 4.80 (dd, J = 17.2, 7.6 Hz, 1H), 4.12 (dd, J = 18.6, 1.8 Hz, 1H), 2.29 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 143.2, 136.3, 134.1, 133.4, 130.6, 129.0, 128.9, 128.8, 128.2, 127.3, 125.8, 125.2, 123.8, 123.1, 120.3, 120.1, 113.7, 109.3, 50.4, 41.2, 21.5. HRMS (EI) $[M+Na]^+$ *m/z* calcd for $C_{25}H_{22}N_2NaO_2S$ 437.1294, found 437.1301.

Full Data of Optimization Studies

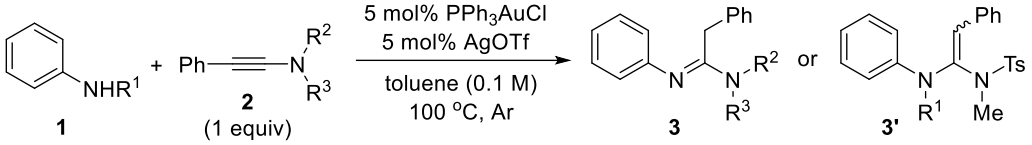
1. Step 1 – Amidine Synthesis: Screening of Additives



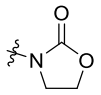
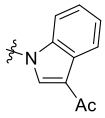
Entry	Additive	Time (h)	**3ad** (%)[a]	Entry	Additive	Time (h)	**3ad** (%)[a]
1	M_2CO_3 (M = Na, K, Cs), NaOAc, K_3PO_4, NEt_3, DMAP, or DBU	24	trace	15	$FeCl_3$	24	64
2	*p*TsOH, AcOH, $BF_3{\cdot}Et_2O$	24	58-60	16	$Fe(OTf)_2$	1	(84)
3	CF_3CO_2H	24	20	17	$CuCl_2$	20	31
4	$HNTf_2$	2	55	18	$Cu(OTf)_2$	3	71
5	TfOH	1.5	63	19	$Cu(OAc)_2$	24	43
6	$AgSbF_6$	10	80 (79)	20	CuCl	24	56
7	$AgPF_6$	10	57	21	CuOTf	1	62
8	AgOTf	2	63	22	CuOAc	24	60
9	$ZnBr_2$	24	76 (71)	23	$Mg(OTf)_2$	24	55
10	$Zn(OTf)_2$	2	54	24	$Bi(OTf)_3$	1	67
11	PPh_3AuCl	24	38	25	$In(OTf)_3$	1	(72)
12	5% PPh_3AuCl / 5% $AgNTf_2$	2	97 (93)	26	$Sc(OTf)_3$	2	58
13	5% PPh_3AuCl / 5% AgOTf	1	93 (90)	27	$Yb(OTf)_3$	2	68 (63)
14	5% PPh_3AuCl / 5% AgOTf	48	77				

In most reactions, a hydrolyzed product of ynamide **2a** was produced in 10~20% yields. [a] Determined by ^1H NMR using trichloroethylene as an internal standard. Values in parentheses indicate isolated yields.

2. Step 1 – Amidine Synthesis: Screening of *N*-Protecting Groups

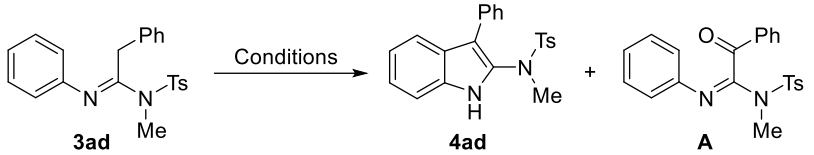


1 + **2** (1 equiv) → **3** or **3'**

With **2d** (R^2 = Ts, R^3 = Me)[a]				With **1a** (R^1 = H)[b]				
Entry	R^1	Time (h)	**3′** (%)[c]	Entry	R^2	R^3	Time (h)	**3** (%)[c]
1	Me	3	(85)	8	Ts	Me (**2d**)	1, 3[d]	(90, 82[d]) (**3ad**)
2	Bn	3	(72)	9	Ts	Bn (**2c**)	3	(80) (**3ac**)
3	Ts	3	(45)	10	Ms	Me (**2b**)	2	(85) (**3ab**)
4	Ms	3	(50)	11	Ms	Bn (**2a**)	2, 2[d]	(85, 76[d]) (**3aa**)
5	Ac	24	0	12	CO_2Me	Bn	2	13
6	Cbz	20	0	13		(**2e**)	2	(85) (**3ae**)
7	Boc	6	0	14			4	(67)
				15			3	(72)

[a] Hydrolyzed product of ynamide **2a** was produced in 4-59% yields. [b] Hydrolyzed product of ynamide **2** was not observed. [c] Determined by ^{1}H NMR using trichloroethylene as an internal standard. Values in parentheses indicate isolated yields. [d] In THF instead of toluene.

3. Step 2 – Indole Synthesis: Cyclization Reaction Under the Conditions (for Oxidative Cyclization of Enamines/Imines) Reported in the Literature



Entry	Reaction Conditions	**4ad** (%)[a]	**A** (%)[a]	References
1	10 mo% $Pd(OAc)_2$, 3 equiv $Cu(OAc)_2$, 3 equiv K_2CO_3 in DMF (0.08 M) at 80 °C for 24 h under Ar	0	0	F. Glorius, *et al.* *Angew. Chem. Int. Ed.* **2008**, *47*, 7230.
2	10 mo% $Pd(OAc)_2$, 2 equiv nBu$_4$NBr in DMSO (0.2 M) at 60 °C for 24 h under O_2	0	15	N. Yoshikai, *et al.* *J. Am. Chem. Soc.* **2012**, *134*, 9098.
3	10 mo% $Pd(OAc)_2$, 2 equiv $Cu(OAc)_2$ in DMSO (0.2 M) at 80 °C for 24 h under Ar	36 (29)	0	N. Yoshikai, *et al.* *J. Am. Chem. Soc.* **2012**, *134*, 9098.
4	5 mo% CuI, 17.5 mo% 1,10-Phen, 2 equiv Li_2CO_3 in DMF (0.1 M) at 100 °C for 24 h under air	0	46	S. Cacchi, *et al.* *Angew. Chem. Int. Ed.* **2009**, *48*, 8078.
5	1.3 equiv $PhI(OAc)_2$ in DCE (0.1 M) at 25 °C for 7 h and then at 60 °C for 17 h	0	5	K. Zhao, *et al.* *Org. Lett.* **2009**, *11*, 2417.
6	10 mo% $FeCl_3$, 3 equiv $Cu(OAc)_2{\cdot}CuCl_2$, 1.5 equiv K_2CO_3 in DMF (0.1 M) at 120 °C for 6 h under Ar	(45)	(15)	Y.-M. Liang, *et al.* *Chem. Commun.* **2010**, *46*, 2823.

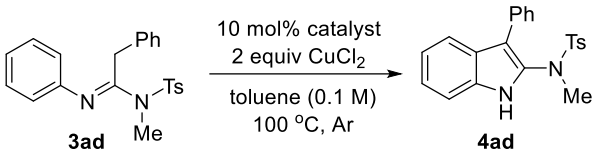
[a] Determined by ^{1}H NMR using trichloroethylene as an internal standard. Values in parentheses indicate isolated yields.

4. Control Experiments of Entry 6 of Above Table

Entry	$FeCl_3$	K_2CO_3	[Cu]	Time (h)	**4ad** (%)[a]	**A** (%)[a]
1	O	O	3 equiv $Cu(OAc)_2{\cdot}CuCl_2$	6	(45)	(15)
2	O	O	3 equiv $CuCl_2$	5	19	12
3	O	X	3 equiv $CuCl_2$	5	(35)	4
4	X	O	3 equiv $CuCl_2$	7	20	10
5	X	X	3 equiv $CuCl_2$	3	(39)	6
6	O	X	3 equiv $Cu(OAc)_2$	4	0	0
7	X	O	3 equiv $Cu(OAc)_2$	7	0	0
8	X	X	3 equiv $Cu(OAc)_2$	4	0	0
9	X	X	1.5 equiv $CuCl_2$	24	22	0
10[b]	X	X	3 equiv $CuCl_2$	5	39	trace
11[b-c]	X	X	3 equiv $CuCl_2$	5	(37)	trace
12[b, d]	X	X	3 equiv $CuCl_2$	24	17	23
13[b-c]	X	X	2 equiv $CuCl_2$	4	34 (32)	5
14[b-c]	X	X	1.5 equiv $CuCl_2$	5	30	11

[a] Determined by ^{1}H NMR using trichloroethylene as an internal standard. Values in parentheses indicate isolated yields. [b] In toluene (0.1 M). [c] At 100 °C. [d] At 60 °C.

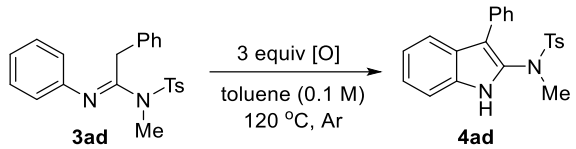
5. Step 2 – Indole Synthesis: Screening of Catalysts



Entry	Catalyst	Time (h)	**4ad** (%)[a]	Entry	Catalyst	Time (h)	**4ad** (%)[a]
1	-	4	34 (32)	8	$IrCl_3$	5	24
2	$FeCl_3$	6	15	9	$[Ru(p\text{-cymene})Cl_2]_2$	5	18
3	$Pd(OAc)_2$	6	18	10	$RuCl_3$	5	33
4[b]	$Pd(OAc)_2$	2	28	11	$AgSbF_6$	6	21
5	$[Cp^*RhCl_2]_2$	5	22	12	$M(OTf)_2$ (M = Cu, Fe)	2	5-9
6	5% $[Cp^*RhCl_2]_2$/10% $AgSbF_6$	4	26	13	10% PPh_3AuCl/10% AgOTf	2	6
7	$[Cp^*IrCl_2]_2$	5	17				

[a] Determined by ^1H NMR using trichloroethylene as an internal standard. Values in parentheses indicate isolated yields. [b] In DMSO (0.2 M) at 120 °C.

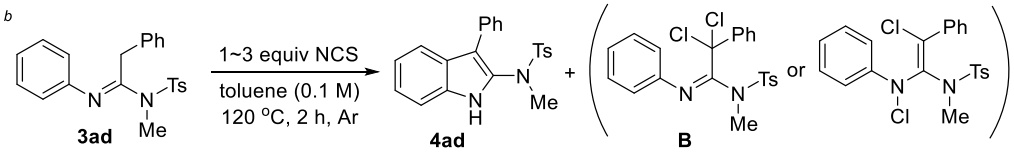
6. Step 2 – Indole Synthesis: Screening of Oxidants

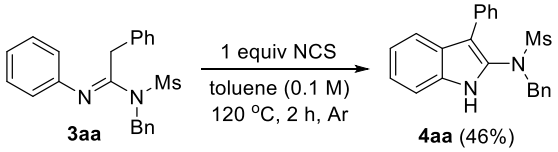


Entry	Oxidant	Time (h)	**4ad** (%)[a]
1	$CuCl_2$	5	39
2	CuX_2 (X = F, Br, OTf, OAc)	2-4	0-trace
3	CuX (X = Br, I, OTf, OAc)	1-24	-
4	AgOAc, Ag_2O, Ag_2CO_3	24	-
5	DDQ, BQ, $K_2S_2O_8$, Oxone, $PhI(OAc)_2$, TBHP, Bz_2O_2, $t\text{Bu}_2O_2$, tBuONO, Selectfluor, $(PhO_2S)_2NF$, $Mn(OAc)_3\cdot 2H_2O$, NBS, NCS[b]	1-24	-
6	I_2	1	20
7	I_2 at 40 °C	24	(27)
8	NIS	3	24
9	40 mol% [I] + 2 equiv TBHP at 60 °C ([I] = I_2, NIS, KI, $n\text{Bu}_4NI$, PhI)	4-20	0-16

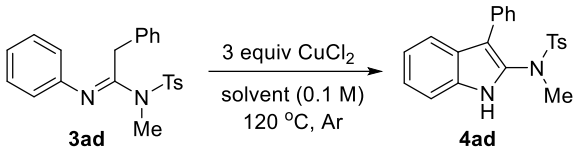
[a] Determined by ^1H NMR using trichloroethylene as an internal standard. Values in parentheses indicate isolated yields.

[b]





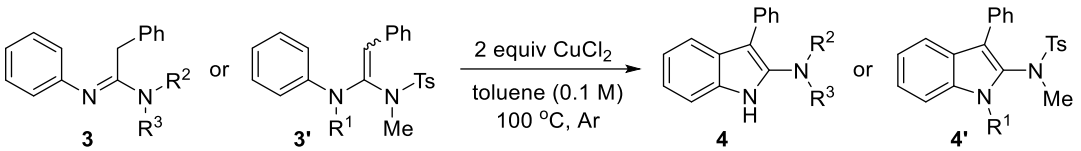
7. Step 2 – Indole Synthesis: Screening of Solvents



Entry	Solvent	Time (h)	**4ad** (%)[a]
1	DMF	3	(39)
2	toluene	5	39
3	$ClCH_2CH_2Cl$	1.5	30
4	1,4-dioxane	5	20
5	THF	1.5	34
6	MeCN	1.5	-
7	EtOAc	3	17
8	DMSO	5	25
9	*t*AmOH	5	5
10	Acetone, EtOH, TFE, HFIP	3-5	-

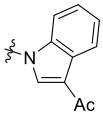
[a] Determined by ^{1}H NMR using trichloroethylene as an internal standard. Values in parentheses indicate isolated yields.

8. Step 2 – Indole Synthesis: Screening of *N*-Protecting Groups



With **3**

Entry	R^2	R^3	Time (h)	**4** (%)[a]
1	Ts	Me (**3ad**)	4	(32) (**4ad**)
2	Ts	Bn (**3ac**)	6	(50) (**4ac**)
3	Ms	Me (**3ab**)	6	(33) (**4ab**)
4	**Ms**	**Bn (3aa)**	**6**	**(73) (4aa)**
5[b]	Ms	Bn (**3aa**)	2	(46) (**4aa**)

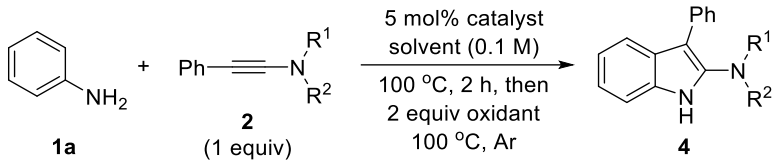
Entry	R^2-R^3	Time (h)	**4** (%)[a]
6	 (**3ae**)	3	11 (**4ae**)
7		4	-
8		5	25

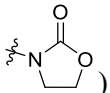
With **3′**

Entry	R^1	Time (h)	**4′** (%)[a]
9	Me	24	-
10	Bn	3	20
11	Ms	24	-

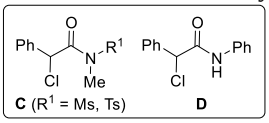
[a] Determined by ^{1}H NMR using trichloroethylene as an internal standard. Values in parentheses indicate isolated yields. [b] Using 1 equiv NCS instead of $CuCl_2$, at 120 °C.

9. One-Pot Two-Step Reaction for Indole Synthesis

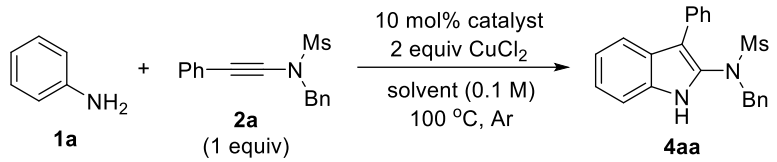


Entry	Variation	Time (h, Step 2)	**4** (%)[a]
	Catalyst (with **2a** (R^1 = Ms, R^2 = Bn), Solvent = toluene, Oxidant = $CuCl_2$)		
1	5 mol% PPh_3AuCl / 5 mol% $AgNTf_2$	4	(45) (**4aa**)
2	**5 mol% PPh_3AuCl / 5 mol% AgOTf**	**4** or 22	**(60)** or (58)
3	10 mol% $AgSbF_6$	2	31
4	10 mol% AgOTf	10	17
5	10 mol% $Cu(OTf)_2$	3	2
	Oxidant (with **2a**, Catalyst = 5 mol% PPh_3AuCl/AgOTf, Solvent = toluene)		
6	**$CuCl_2$**	**4**	**(60)** (**4aa**)
7	I_2	2	6
8	NIS	2	12
9	NCS (1 or 2 equiv)	4	30 or 7
	Solvent (with **2a**, Catalyst = 5 mol% PPh_3AuCl/AgOTf, Oxidant = $CuCl_2$)		
10	toluene	4	(60) (**4aa**)
11	$ClCH_2CH_2Cl$	4	(44)
12	**THF**	**4**	**(73)**
13	DMF	4	13
14	toluene (0.2 M, step 1) → THF (0.2 M, step 2)	4	(71)
15	toluene (0.2 M, step 1) → DMF (0.2 M, step 2)	4	(59)
	2 (Catalyst = 5 mol% PPh_3AuCl/AgOTf, Oxidant = $CuCl_2$, Solvent = THF)		
16	**2a (R^1 = Ms, R^2 = Bn)**	**4**	**(73)** (**4aa**)
17[b]	**2b** (R^1 = Ms, R^2 = Me)	6	35 (**4ab**)
18	**2c** (R^1 = Ts, R^2 = Bn)	6	(69) (**4ac**)
19[b]	**2d** (R^1 = Ts, R^2 = Me)	6	30 (**4ad**)
20	(R^1 = Ms, R^2 = *n*Bu)	6	60
21	(R^1 = Ms, R^2 = *c*Hex, Ph, or *p*Tol)	6	36-42
22	(R^1 = Ms, R^2 = *t*Bu or allyl)	6	-
23	(R^1-R^2 = )	6	- (**4ae**)
	Other variation from the conditions of entry 11		
24	1.5 equiv **2a**	4	(76) (**4aa**)
25	2% PPh_3AuCl / 2% AgOTf	4	(66)
26	under air	4	(68)

[a] Determined by ^{1}H NMR using trichloroethylene as an internal standard. Values in parentheses indicate isolated yields. [b] **C** and **D** were obtained in 18-25% and 13-28% yields, respectively.

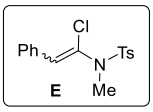


10. One-Pot Reaction for Indole Synthesis

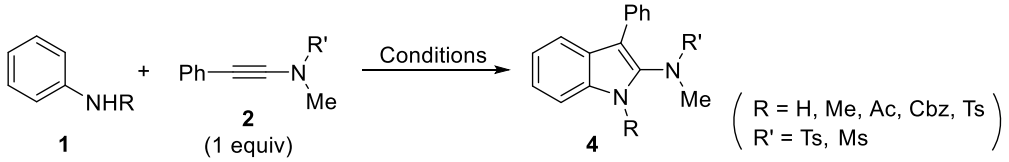


Entry	Catalyst	Solvent	Time (h)	**4aa** (%)[a]
1	-	toluene	24	-[b]
2	5 mol% PPh_3AuCl/AgOTf (1:1)	toluene	24	26
3	5 mol% PPh_3AuCl/AgOTf (1:1)	THF	24	12
4	5 mol% PPh_3AuCl/AgOTf (1:1)	toluene/DMF (1:1)	24	5
5	5 mol% PPh_3AuCl/$AgNTf_2$ (1:1)	toluene	24	33
6	$AgSbF_6$	toluene	2	38
7	AgOTf	toluene	19	17
8	$Cu(OTf)_2$	toluene	7	7
9	$Yb(OTf)_3$	toluene	7	9
10	$In(OTf)_3$	toluene	7	4
11	$Fe(OTf)_2$	toluene	19	-
12	$FeCl_3$	toluene	19	-
13	$ZnBr_2$	toluene	19	trace

[a] Determined by ^1H NMR using trichloroethylene as an internal standard. [b] **E** was obtained in 52% yields with *Z*/*E* = 1/1.



11. One-Pot Reaction Using the Indole Forming Protocols (Intermolecular Coupling of Amines/Amides with Alkynes/Alkenes) Reported in the Literature

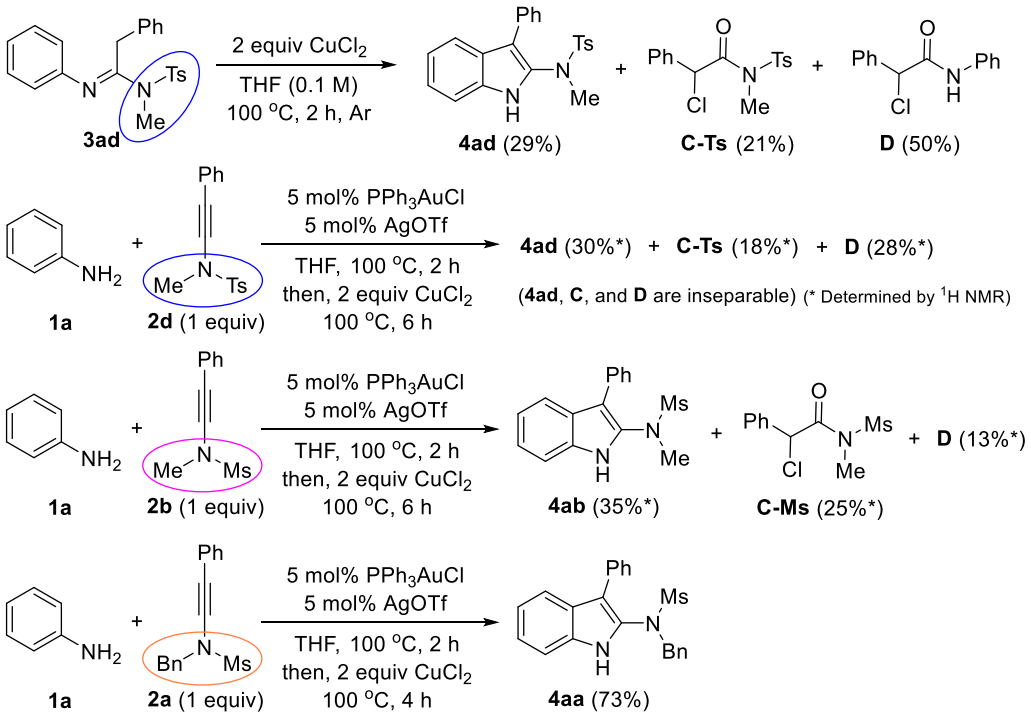


Entry	Reaction Conditions	R	**4** (%)[a]	References
	R′ = Ms			
1	2.5 mol% $[Cp^*RhCl_2]_2$, 10 mol% $AgSbF_6$, 2.1 equiv $Cu(OAc)_2·H_2O$ in *t*AmOH (0.2 M) at 120 °C for 12-24 h under air	H	20	K. Fagnou, *et al*. *J. Am. Chem. Soc*. **2008**, *130*, 16474.
		Me, Ac, Cbz, Ts	-	
2	5 mo% $Pd(OAc)_2$, 10 mol% BPhen, 2 equiv $Cu(OAc)_2·H_2O$, 0 or 1 equiv BQ in toluene (0.1 M) at 120 °C for 18-24 h under air	H, Me, Ac, Cbz, Ts	-	S. W. Youn, *et al*. *Angew. Chem. Int*. *Ed*. **2017**, *56*, 6636.
3	5 mo% $Pd(OAc)_2$, 2 equiv $Cu(OAc)_2·H_2O$, 0 or 2 equiv NaOAc in toluene (0.1 M) at 120 °C for 2-18 h under air (modified)	H, Ts	-	A. K. Sahoo, *et al*. *Angew. Chem. Int*. *Ed*. **2013**, *52*, 4607.
4	0 or 5 mo% $Pd(OAc)_2$, 2 equiv K_2CO_3 in toluene (0.1 M) at 120 °C for 24 h under air	H	-	T. Skrydstrup, *et al*. *J. Org. Chem.* **2008**, *73*, 9447.
	R′ = Ts			
5	5 mo% $Pd(OAc)_2$ in DMA/PivOH (4/1, 0.2 M) at 120 °C for 10 h under O_2	H	-	N. Jiao, *et al*. *Angew. Chem. Int*. *Ed*. **2009**, *48*, 4572.
6	10 mo% $Pd(OAc)_2$, 2 equiv $Cu(OAc)_2$ in DMSO (0.2 M) at 80 °C for 24 h under Ar	H	-	N. Yoshikai, *et al*. *J. Am. Chem. Soc*. **2012**, *134*, 9098.
7	5 mol% $[Cp^*RhCl_2]_2$, 2 equiv NaOAc in toluene (0.25 M) at 120 °C or in MeOH (0.25 M) at 25 °C for 12-24 h under air	H, Me, Ac, Cbz, Ts	-	J. You, *et al.* *RSC Adv*. **2014**, *4*, 49186.
8	2.5 mol% $[Cp^*RhCl_2]_2$, 25 mol% CsOAc, 1.2 equiv AcOH in toluene (0.4 M) at 120 °C or in CH_2Cl_2 (0.4 M) at 25 °C for 24 h under Ar	H, Me, Ac, Cbz, Ts	-	G. Liu, X. Lu, *et al*. *Angew. Chem. Int. Ed*. **2013**, *52*, 6033.
9	2.5 mol% $[Ru(p\text{-cymene})Cl_2]_2$, 25 mol% K_2CO_3 in toluene (0.4 M) at 120 °C or in CH_2Cl_2 (0.4 M) at 25 °C for 24 h under Ar	H, Me, Ac, Cbz, Ts	-	G. Liu, X. Lu, *et al*. *Org. Chem. Front.* **2014**, *1*, 1161.

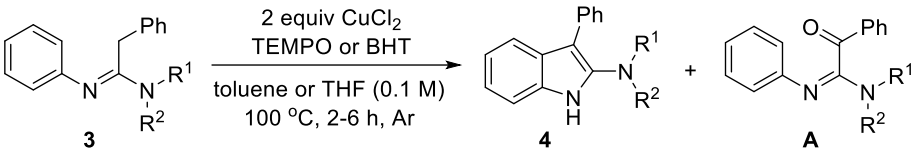
[a] Isolated yields.

Mechanistic Studies for Step 2

1. Byproducts as a Possible Intermediate



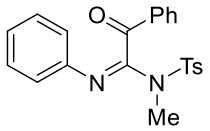
2. Reactions of 3 in the Presence of Radical Scavenger



Entry	**3** (R^1, R^2)	Radical Scavenger	Solvent	Time (h)	**4** (%)[a]	**A** (%)[a]
1	**3ad** (Ts, Me)	-	toluene	4	(32) (**4ad**)	5
2[b]		-	THF	1.5	34	-
3		TEMPO (1 equiv)	THF	2	39	30
4		BHT (1 equiv)	THF	2	15	-
5	**3aa** (Ms, Bn)	-	toluene	6	(73) (**4aa**)	-
6		TEMPO (1 equiv)	THF	6	69	31
7		TEMPO (3 equiv)	THF	6	-	(65)
8		BHT (1 equiv)	THF	6	43	-
9		BHT (3 equiv)	THF	6	32	-

[a] Determined by ^{1}H NMR using trichloro-ethylene as an internal standard. Values in parentheses indicate isolated yields. [b] 3 equiv $CuCl_2$ at 120 °C.

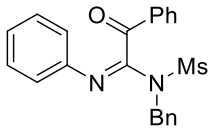
(*E*)-*N*-Methyl-2-oxo-*N′*,2-diphenyl-*N*-tosylacetimidamide (A-Ts)



15% (6.1 mg). a white solid (EtOAc : *n*-Hexane = 1:6), mp 130-132 °C.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.87 (d, J = 8.4 Hz, 2H), 7.76 (d, J = 7.6 Hz, 2H), 7.46 (t, J = 7.4 Hz, 1H), 7.40 (d, J = 8.0 Hz, 2H), 7.35 (t, J = 7.8 Hz, 2H), 7.02 (t, J = 7.8 Hz, 2H), 6.83 (t, J = 7.4 Hz, 1H), 6.62 (d, J = 7.6 Hz, 2H), 3.32 (s, 3H), 2.48 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 189.8, 152.8, 146.1, 144.9, 135.1, 134.5, 133.7, 129.9, 129.2, 128.4, 128.0, 123.7, 120.9, 33.2, 21.7 (1 carbon is missing due to overlapping). LCMS *m/z* 393 $[M+H]^+$. HRMS (EI) $[M]^+$ *m/z* calcd for $C_{22}H_{20}N_2O_3S$ 392.1189, found 392.1189.

(*E*)-*N*-Benzyl-*N*-(methylsulfonyl)-2-oxo-*N′*,2-diphenylacetimidamide (A-Ms)

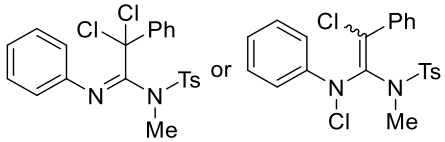


65% (13.8 mg). a yellow oil (EtOAc : *n*-Hexane = 1:4).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.62 (d, J = 7.6 Hz, 2H), 7.55 (d, J = 7.6 Hz, 2H), 7.42-7.34 (m, 4H), 7.25 (t, J = 7.6 Hz, 2H), 6.99 (t, J = 7.6 Hz, 2H), 6.79 (t, J = 7.4 Hz, 1H), 6.59 (d, J = 7.6 Hz, 2H), 5.34 (br s, 2H), 2.98 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 191.0, 151.6, 145.6, 135.8, 134.4, 133.8, 129.4, 128.7, 128.4, 128.3, 128.2, 128.0, 123.8, 120.7, 48.8, 42.7. LCMS *m/z* 393 $[M+H]^+$.

Spectral data were consistent with data reported in the literature.[1]

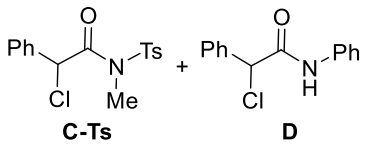
(*E*)-2,2-Dichloro-*N*-methyl-*N′*,2-diphenyl-*N*-tosylacetimidamide or *N*-(2-chloro-1-(chloro(phenyl)-amino)-2-phenylvinyl)-*N*,4-dimethylbenzenesulfonamide (B)



88% (20.7 mg). a white solid (EtOAc : *n*-Hexane = 1:5), mp 112-114 °C.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.90 (d, J = 7.2 Hz, 2H), 7.44-7.36 (m, 3H), 7.23 (t, J = 8.0 Hz, 2H), 7.22 (d, J = 7.6 Hz, 2H), 7.11 (t, J = 7.2 Hz, 1H), 7.07 (d, J = 8.4 Hz, 2H), 6.77 (d, J = 7.6 Hz, 2H), 3.15 (s, 3H), 2.36 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 152.1, 146.6, 143.6, 135.3, 129.19, 129.16, 128.8, 128.1, 127.9, 127.3, 125.2, 119.7, 37.6, 21.5 (2 carbons are missing due to overlapping). LCMS *m/z* 447 $[M+H]^+$. HRMS (EI) $[M]^+$ *m/z* calcd for $C_{22}H_{20}Cl_2N_2O_2S$ 446.0617, found 446.0621.

2-Chloro-*N*-methyl-2-phenyl-*N*-tosylacetamide (C-Ts) & 2-Chloro-*N*,2-diphenylacetamide (D)



C-Ts **D**

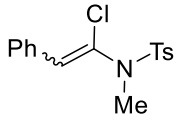
Inseparable mixture of **C-Ts** and **D** (12.2 mg, **C-Ts**:**D** = 1:2.2) was obtained as a white solid (CH_2Cl_2 : *n*-Hexane = 1:1).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.38 (br s, 1H of **D**), 7.57 (t, J = 8.0 Hz, 2H of **C-Ts** & 2H of **D**), 7.51 (dd,

J = 7.8, 1.8 Hz, 2H of **D**), 7.47-7.45 (m, 2H of **C-Ts**), 7.43-7.34 (m, 3H of **C-Ts** & 5H of **D**), 7.28 (d, *J* = 8.4 Hz, 2H of **C-Ts**), 7.17 (t, *J* = 7.4 Hz, 1H of **D**), 6.48 (s, 1H of **C-Ts**), 5.51 (s, 1H of **D**), 3.20 (s, 3H of **C-Ts**), 2.43 (s, 3H of **C-Ts**). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 168.1, 165.3, 145.4, 136.9, 136.7, 135.3, 135.0, 130.0, 129.4, 129.3, 129.1, 129.02, 128.95, 128.6, 127.8, 127.7, 125.2, 120.0, 62.1, 58.6, 33.6, 21.6. LCMS *m*/*z* 338 $[M+H]^+$ of **C-Ts**, 246 $[M+H]^+$ of **D**.

Spectral data of **C-Ts**[20] and **D**[21] were consistent with data reported in the literature.

***N*-(1-Chloro-2-phenylvinyl)-*N*,4-dimethylbenzenesulfonamide (E)**



52% (71.8 mg, *E*:*Z* = 1:1). a white oil (EtOAc : *n*-Hexane = 1:8).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.78 (d, *J* = 8.0 Hz, 2H), 7.76 (d, *J* = 8.0 Hz, 2H), 7.62-7.60 (m, 4H), 7.40-7.29 (m, 10H), 6.92 (s, 1H), 6.66 (s, 1H), 3.09 (s, 3H), 3.04 (s, 3H), 2.45 (s, 3H), 2.44 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 144.4, 144.2, 134.4, 134.1, 133.0, 132.9, 132.3, 130.4, 129.7, 129.6, 129.43, 129.36, 128.8, 128.72, 128.69, 128.6, 128.3, 128.2, 128.1, 35.9, 35.7, 21.6 (2 carbons are missing due to overlapping). LCMS *m*/*z* 322 $[M+H]^+$.

Spectral data of (*E*)-[22] and (*Z*)-isomers[20] were consistent with data reported in the literature.

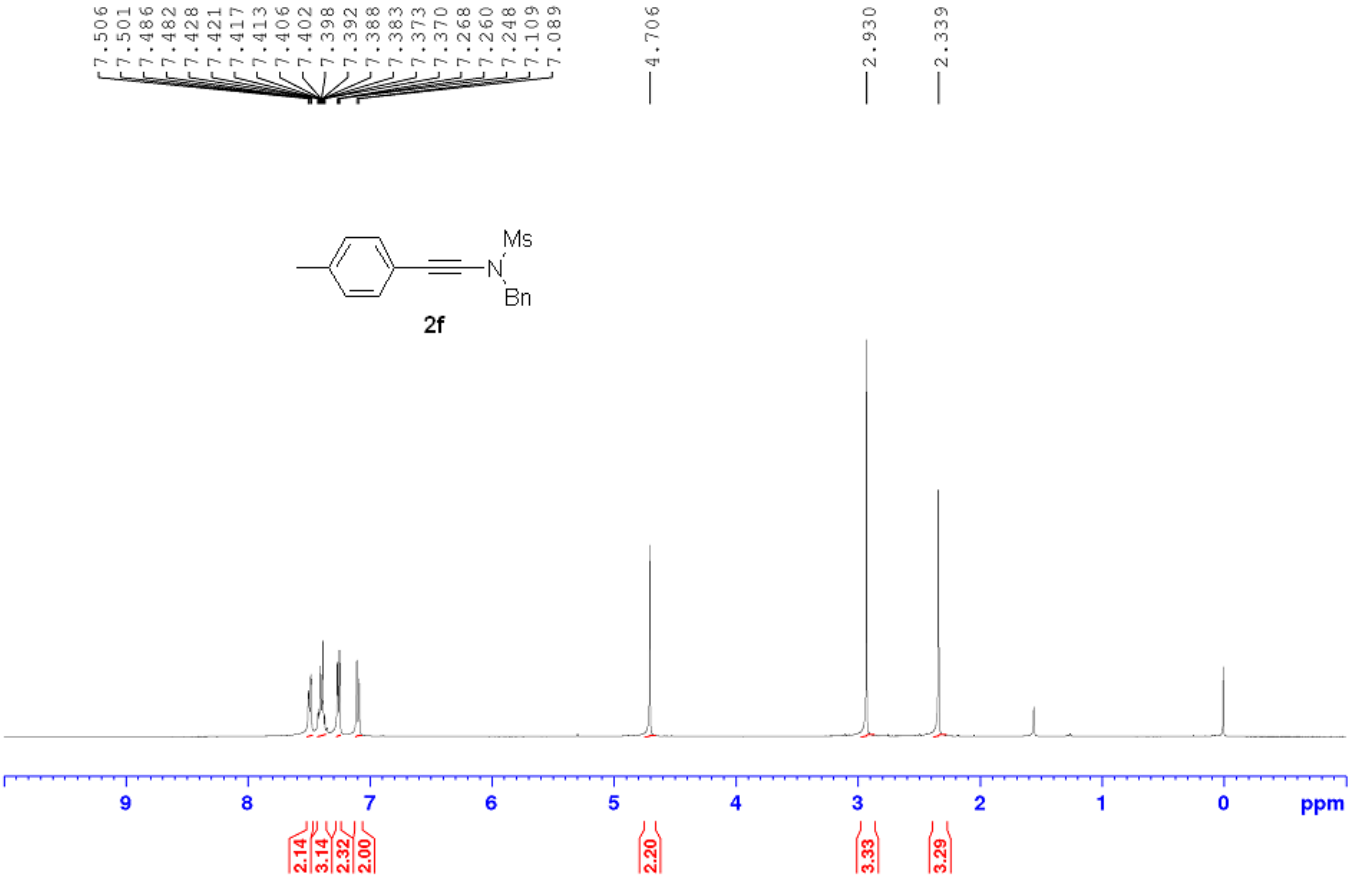
[20] Pan, F.; Li, X.-L.; Chen, X.-M.; Shu, C.; Ruan, P.-P.; Shen, C.-H.; Lu, X.; Ye, L.-W. *ACS Catal.* **2016**, *6*, 6055.

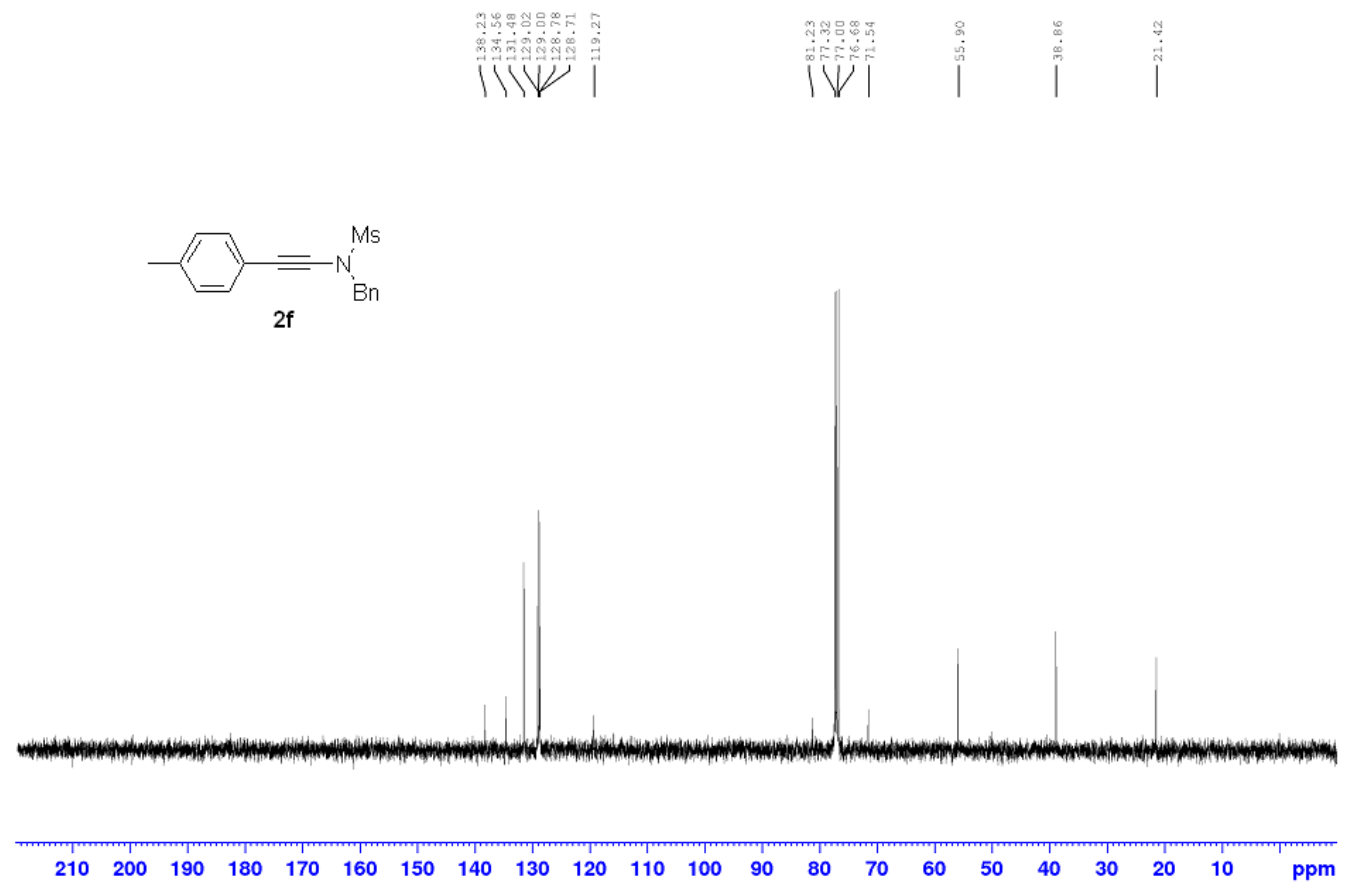
[21] Song, Q.-W.; Yu, B.; Liu, A.-H.; He, Y.; Yang, Z.-Z.; Diao, Z.-F.; Song, Q.-C.; Li, X.-D.; He, L.-N. *RSC Adv.* **2013**, *3*, 19009.

[22] Kim, S. W.; Um, T.-W.; Shin, S. *Chem. Commun.* **2017**, *53*, 2733.

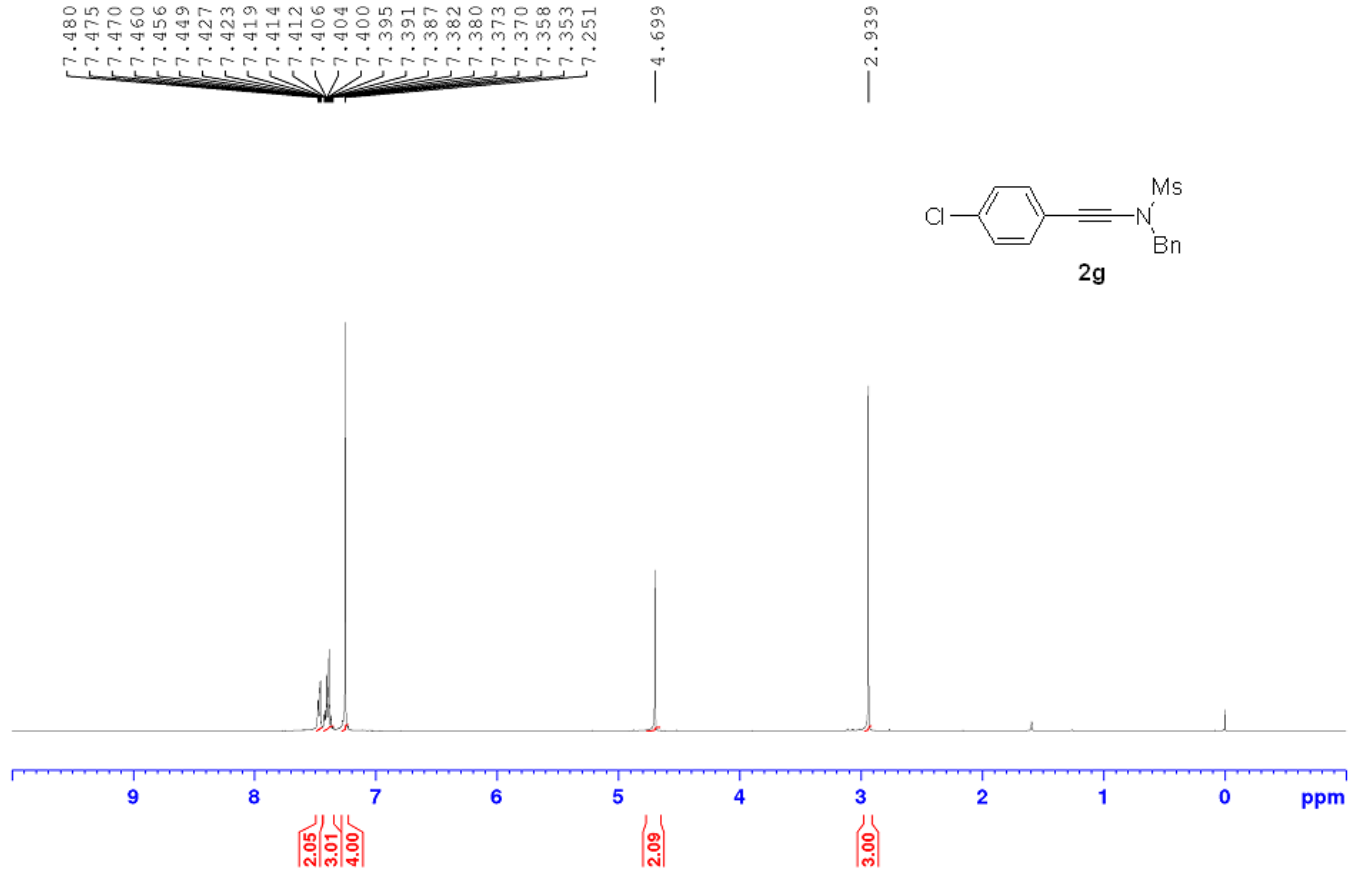
Copies of NMR Spectra

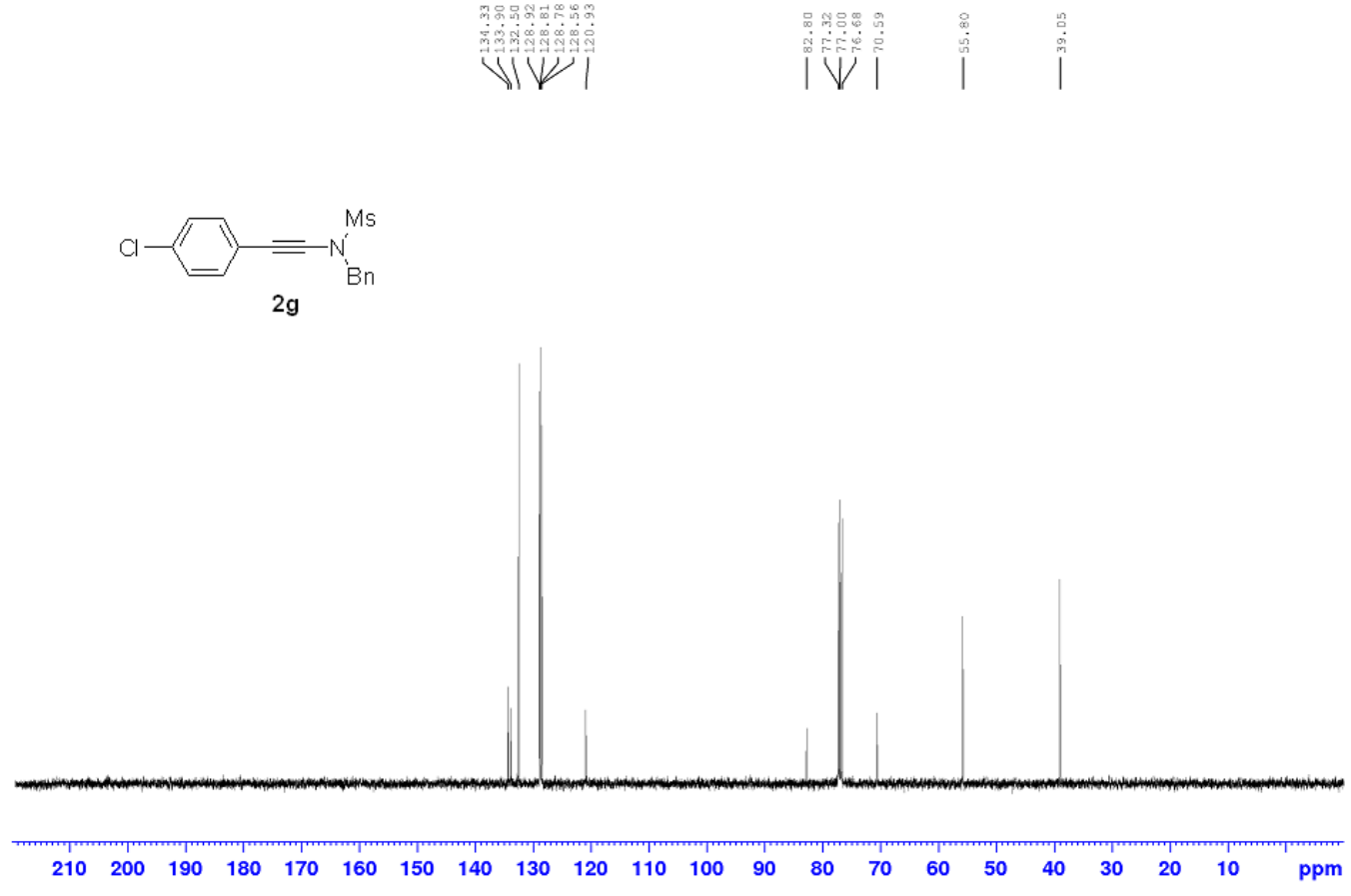
N-Benzyl-*N*-(*p*-tolylethynyl)methanesulfonamide (2f)



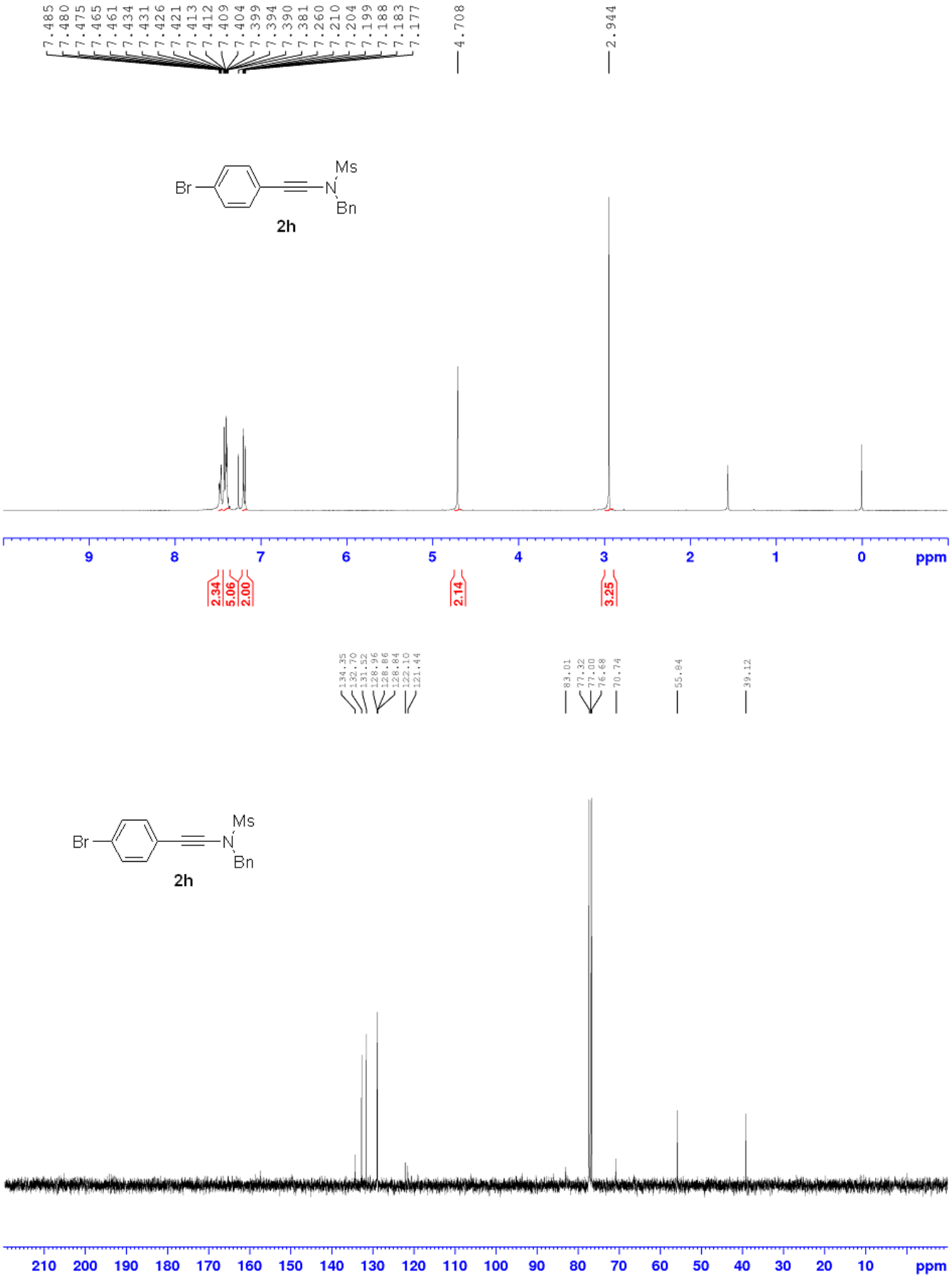


_N_-Benzyl-_N_-((4-chlorophenyl)ethynyl)methanesulfonamide (2g)

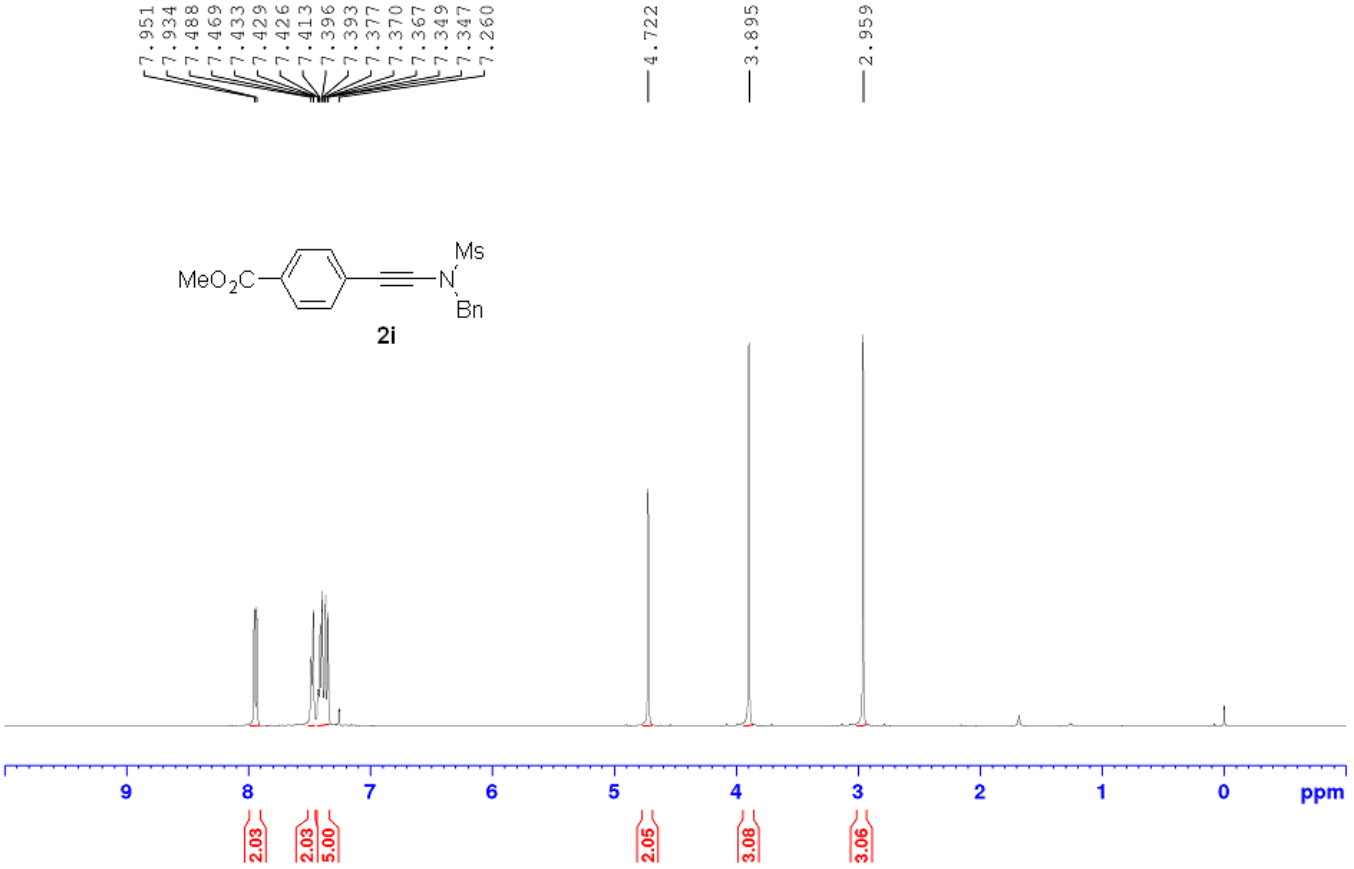


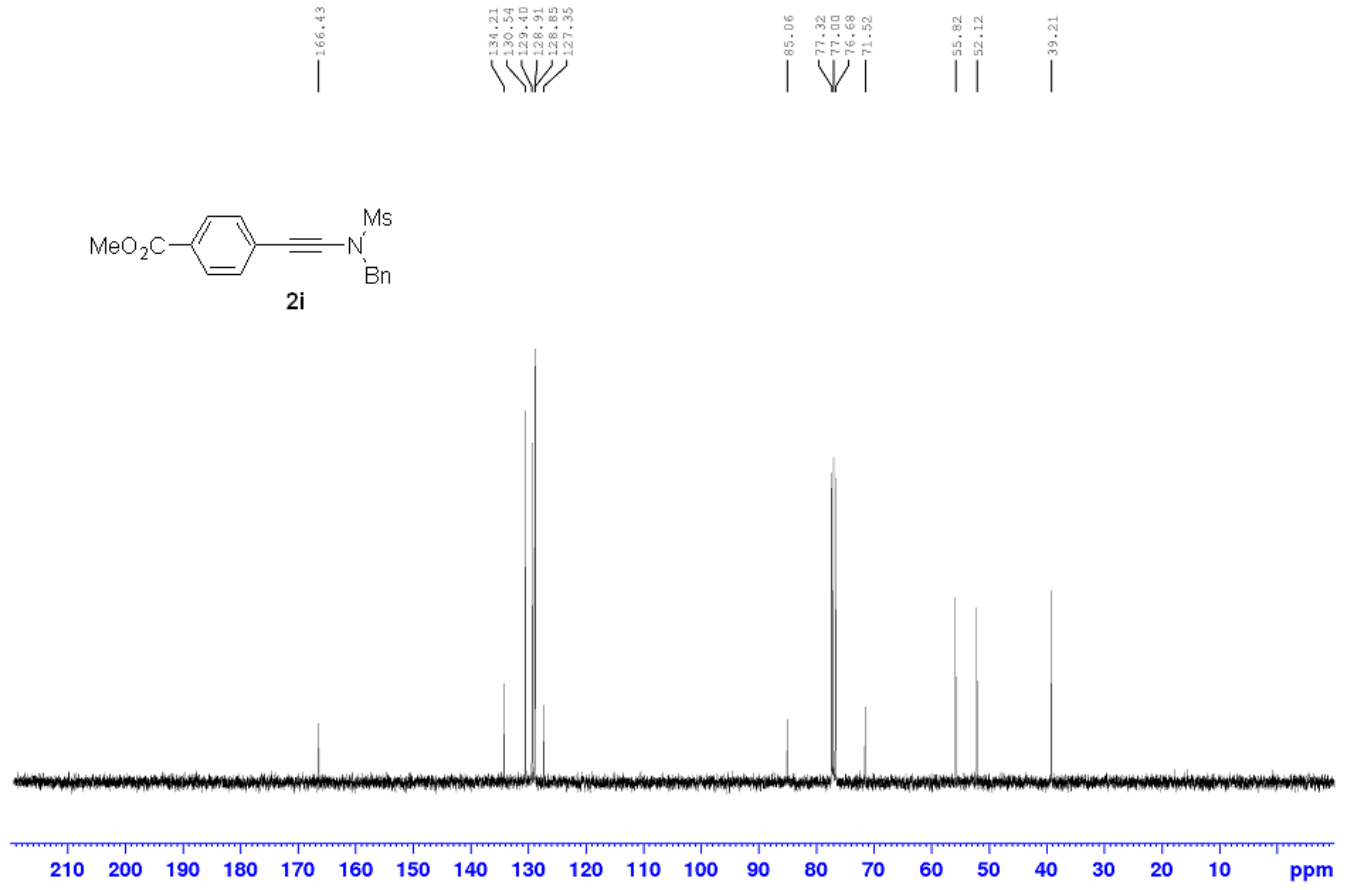


_N_-Benzyl-_N_-((4-bromophenyl)ethynyl)methanesulfonamide (2h)

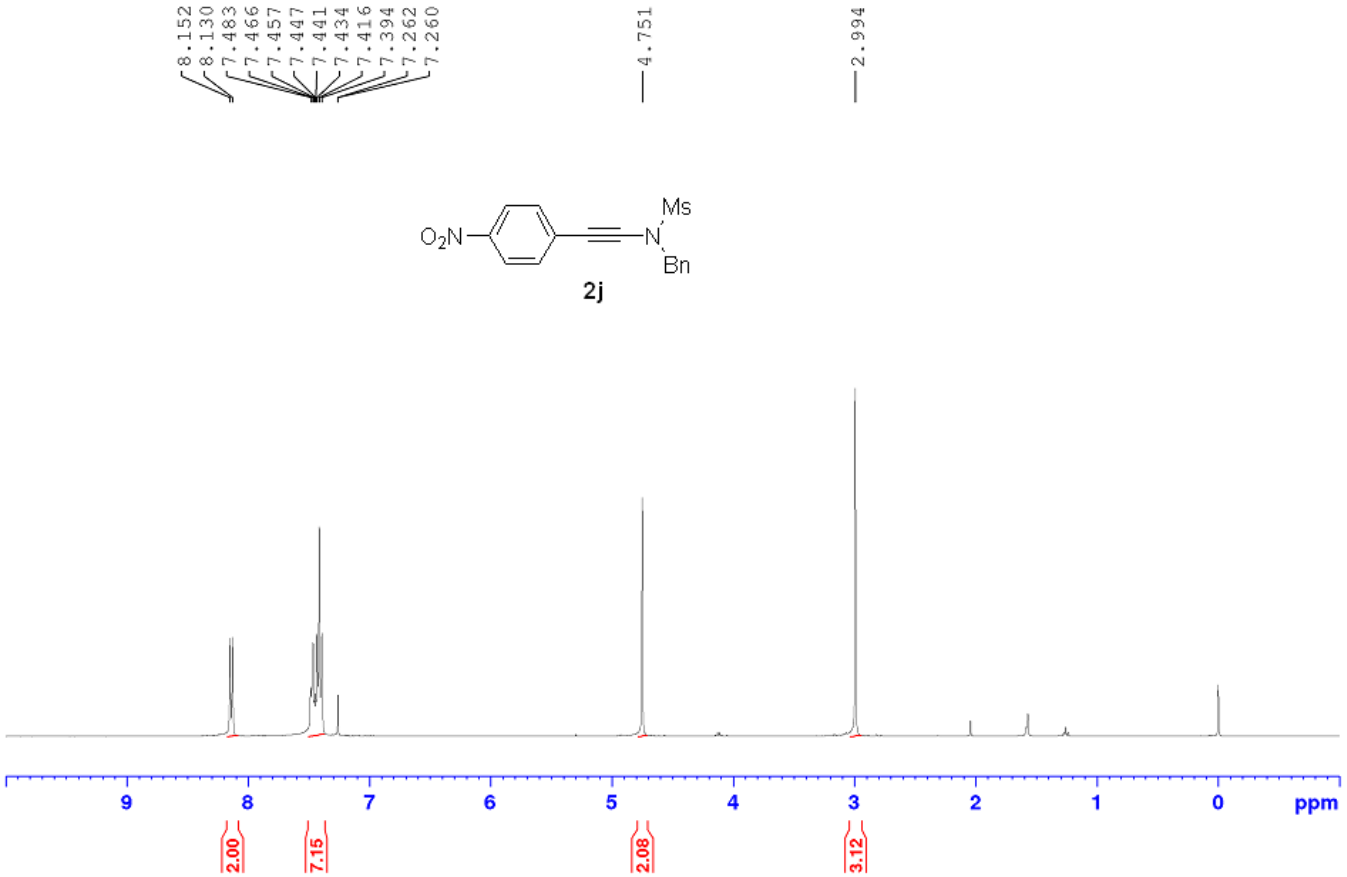


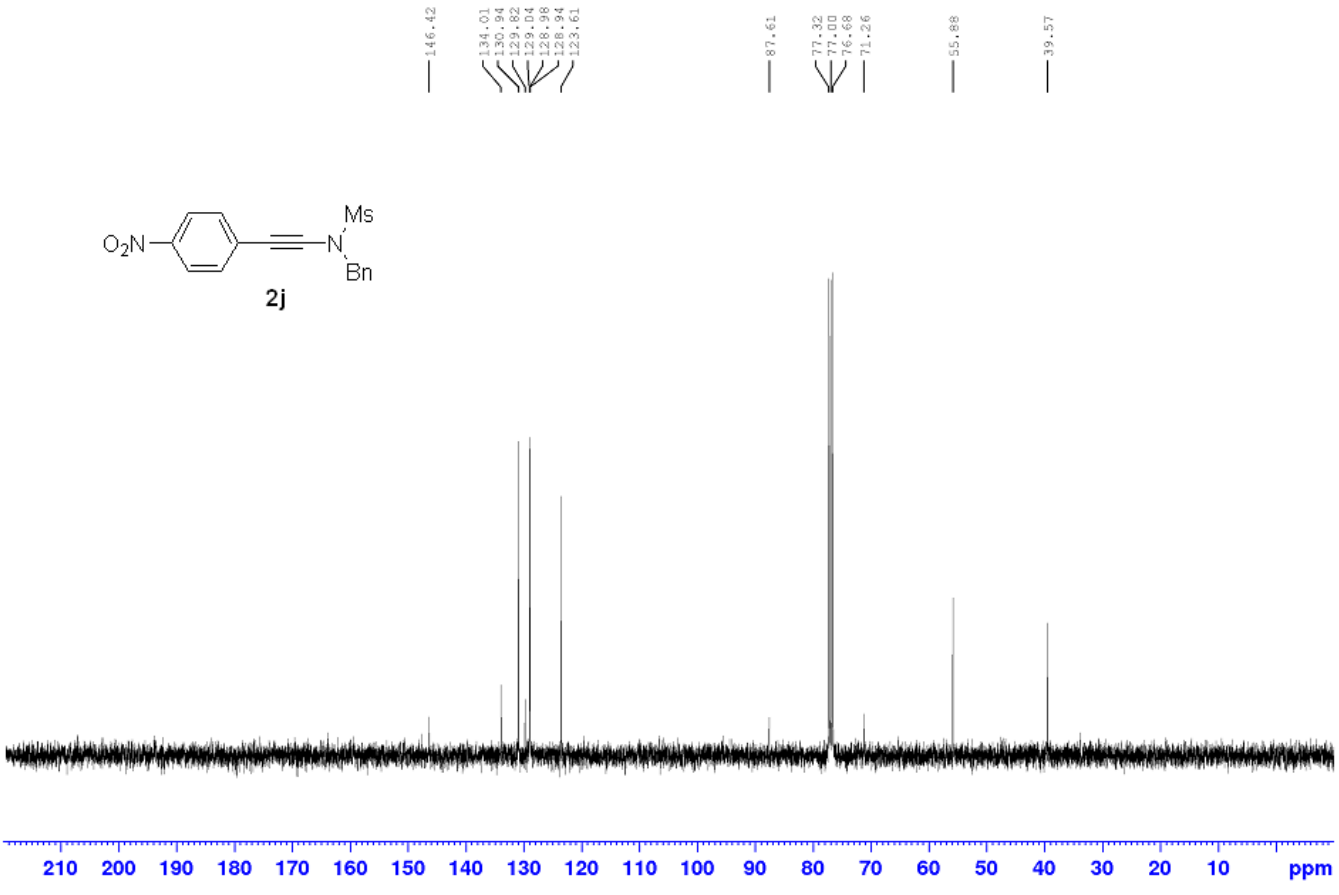
Methyl 4-((*N*-Benzylmethylsulfonamido)ethynyl)benzoate (2i)



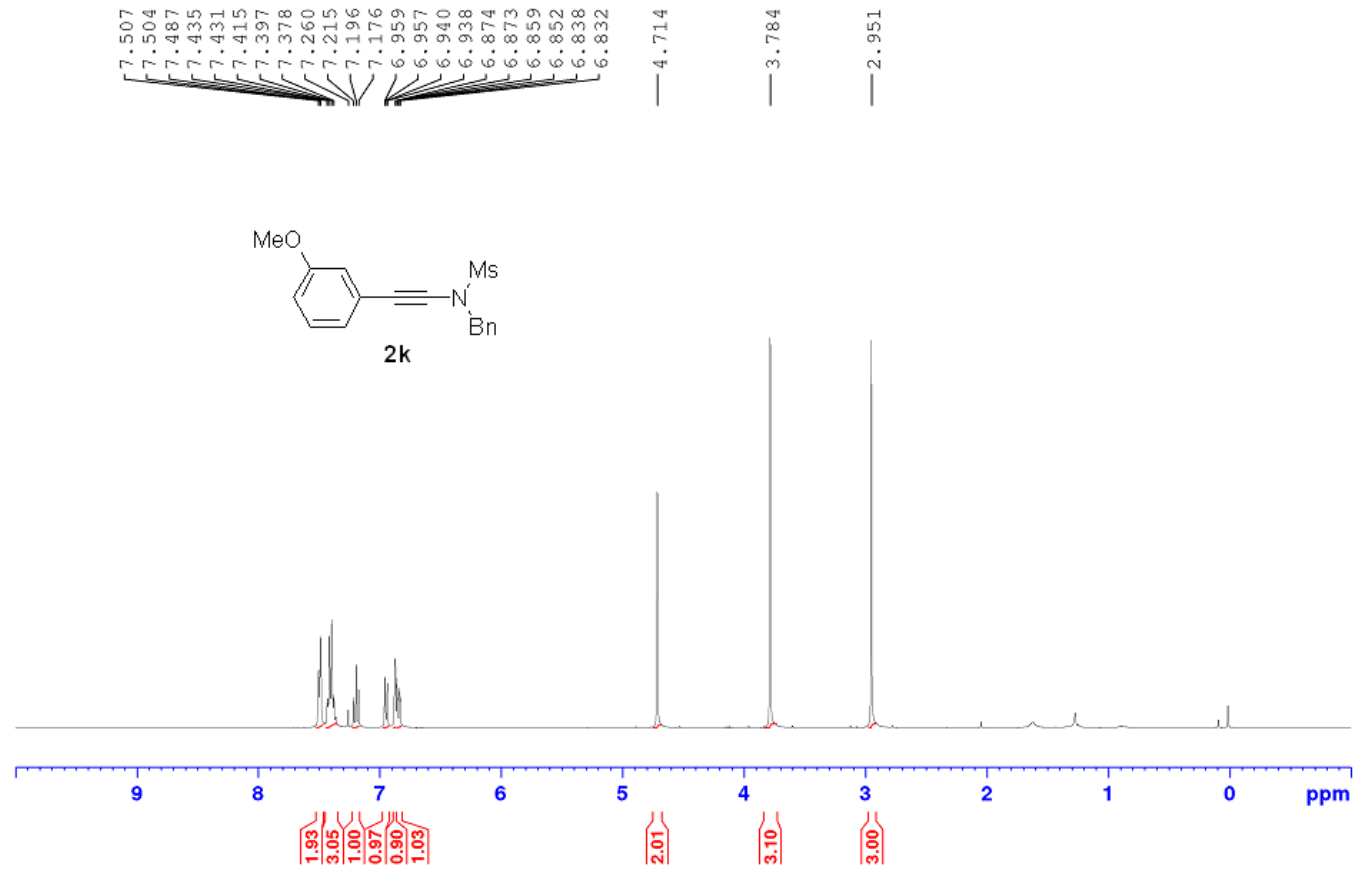


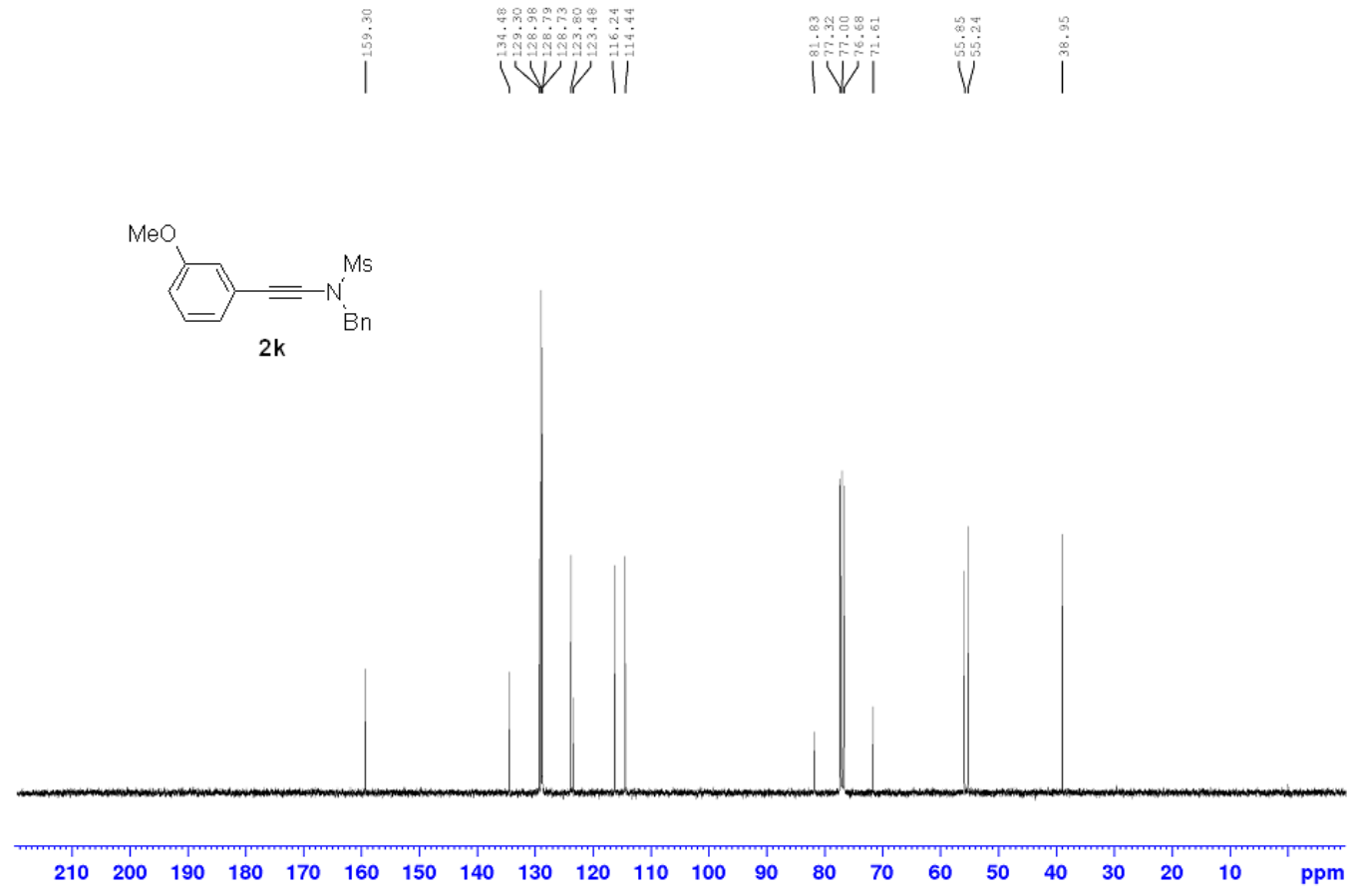
_N_-Benzyl-_N_-((4-nitrophenyl)ethynyl)methanesulfonamide (2j)



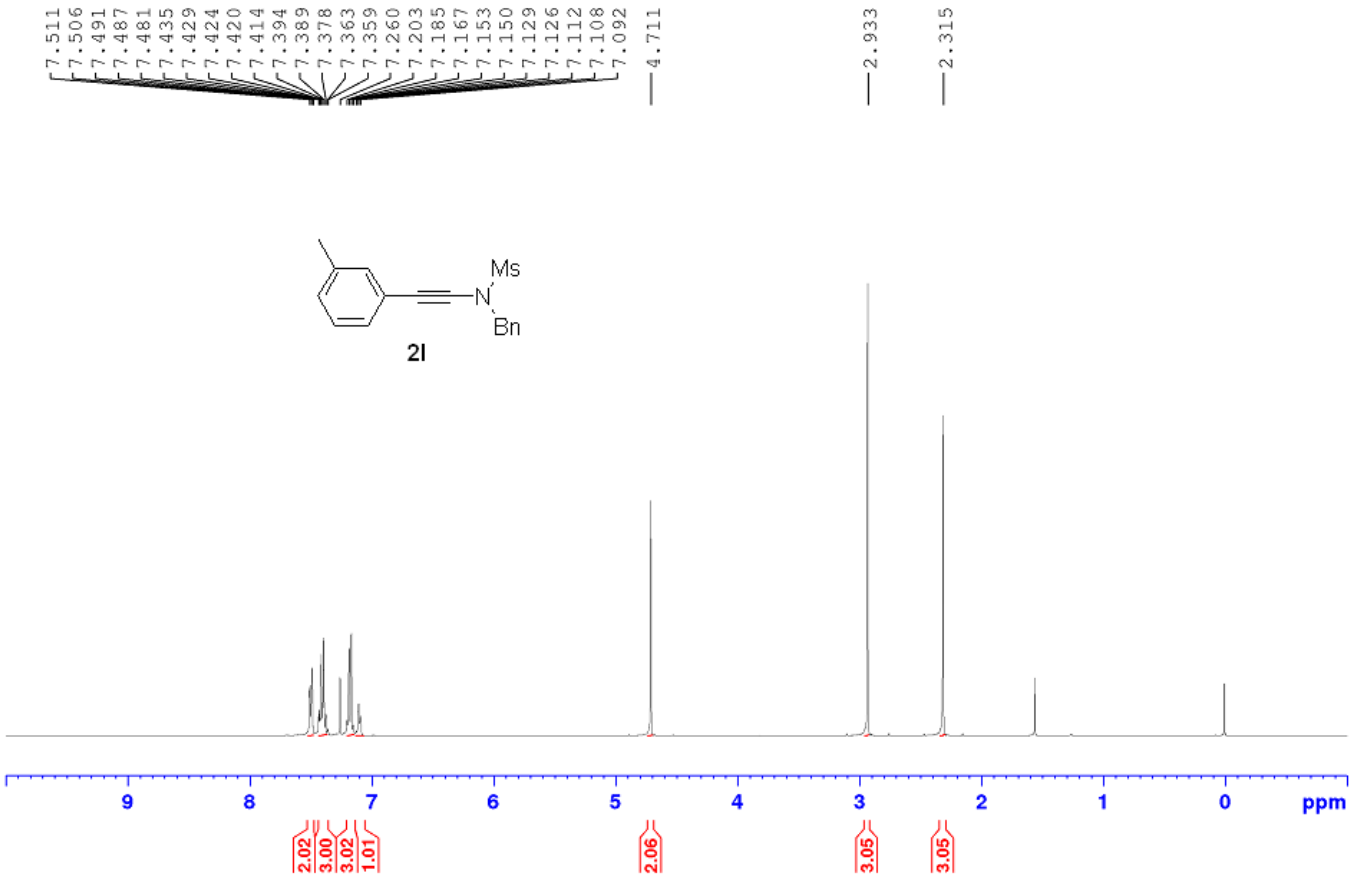


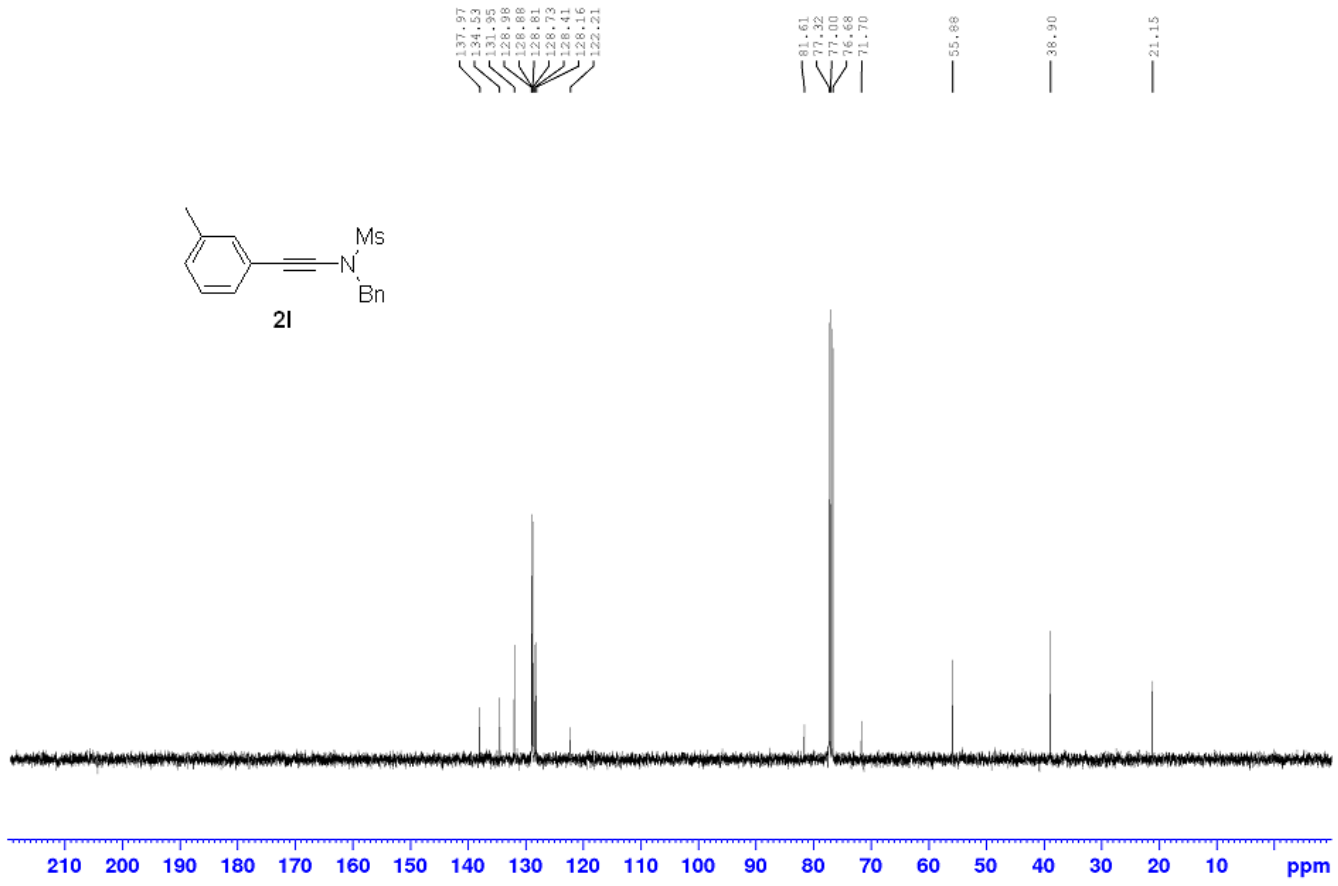
_N_-Benzyl-_N_-((3-methoxyphenyl)ethynyl)methanesulfonamide (2k)



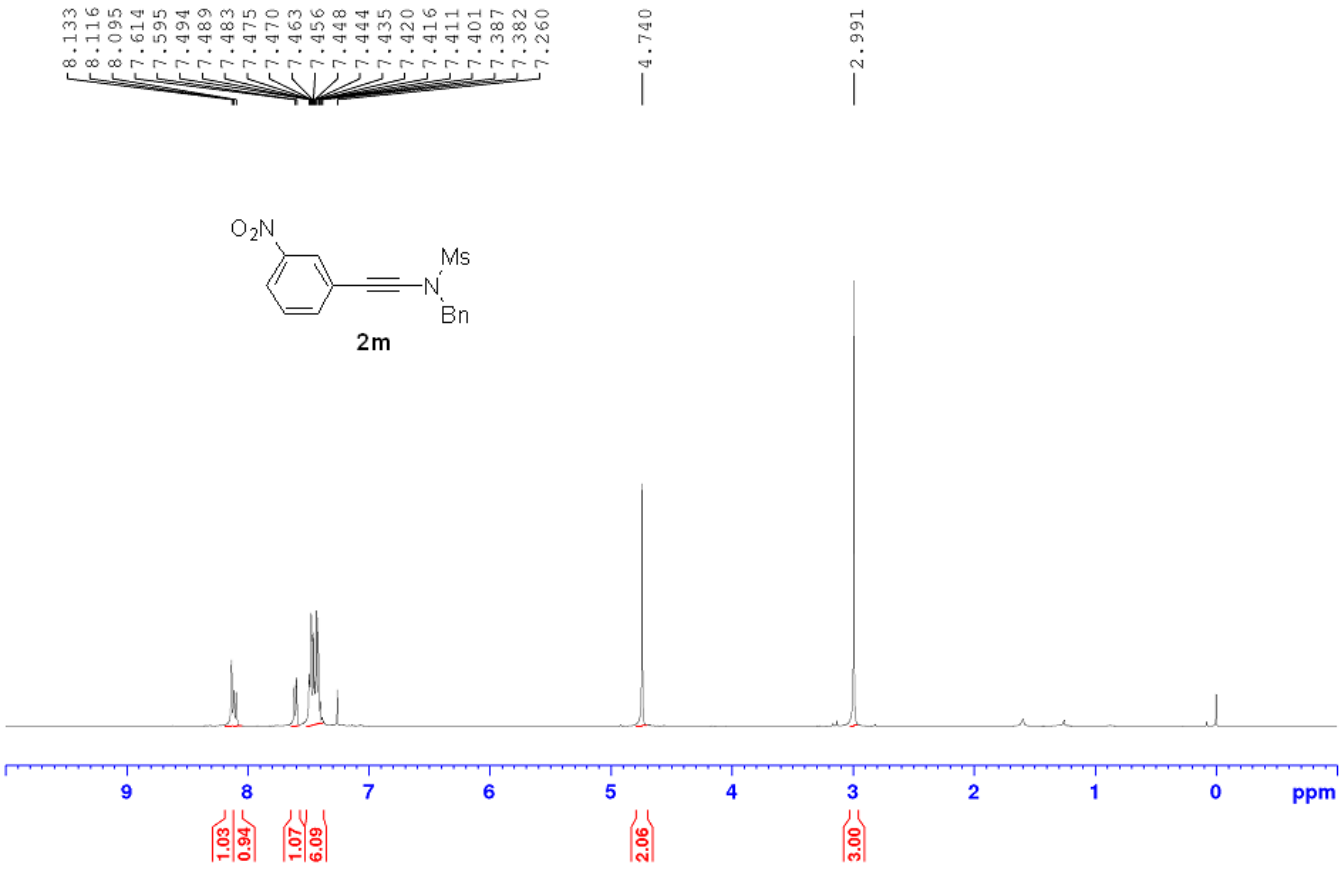


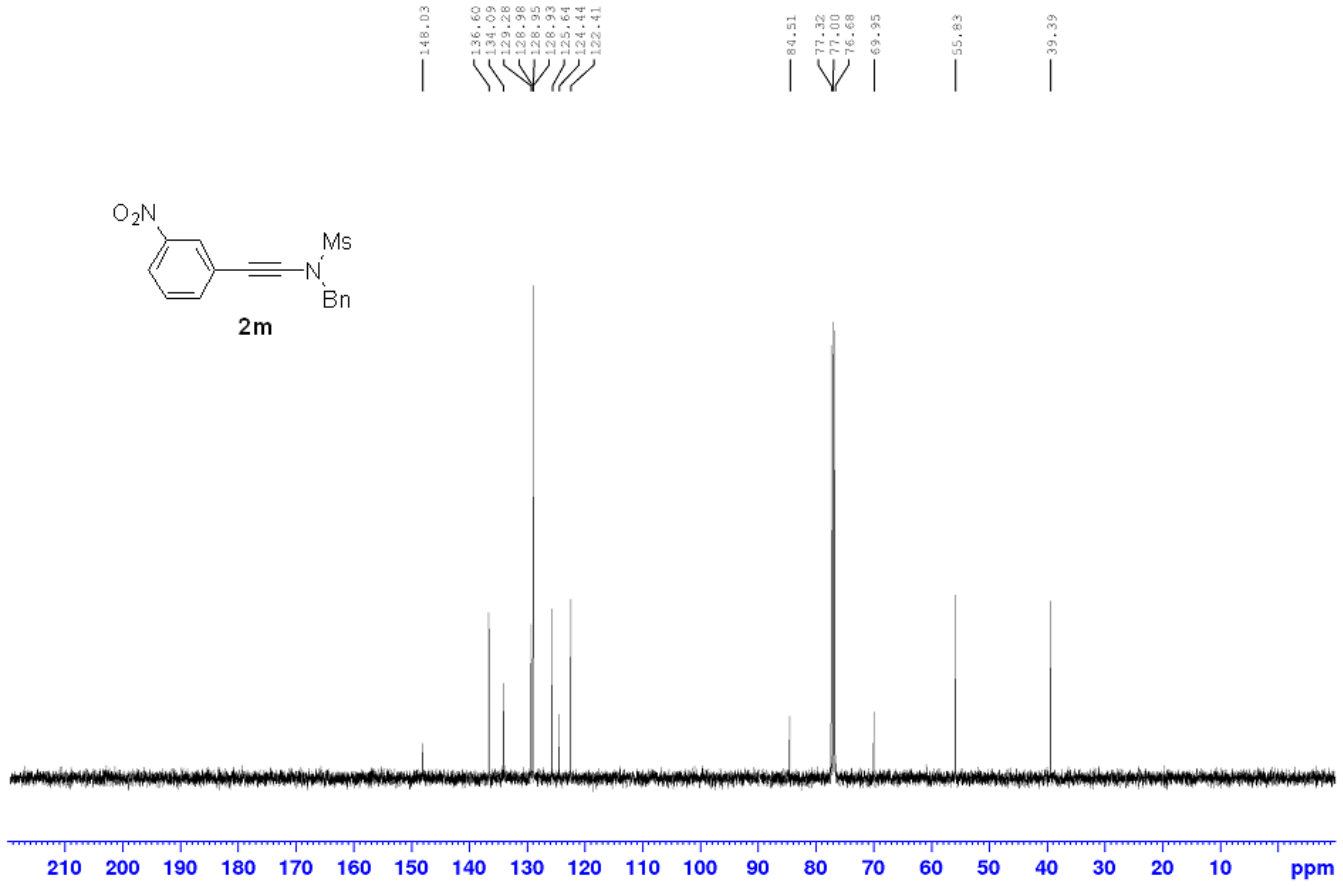
_N_-Benzyl-_N_-(_m_-tolylethynyl)methanesulfonamide (2l)



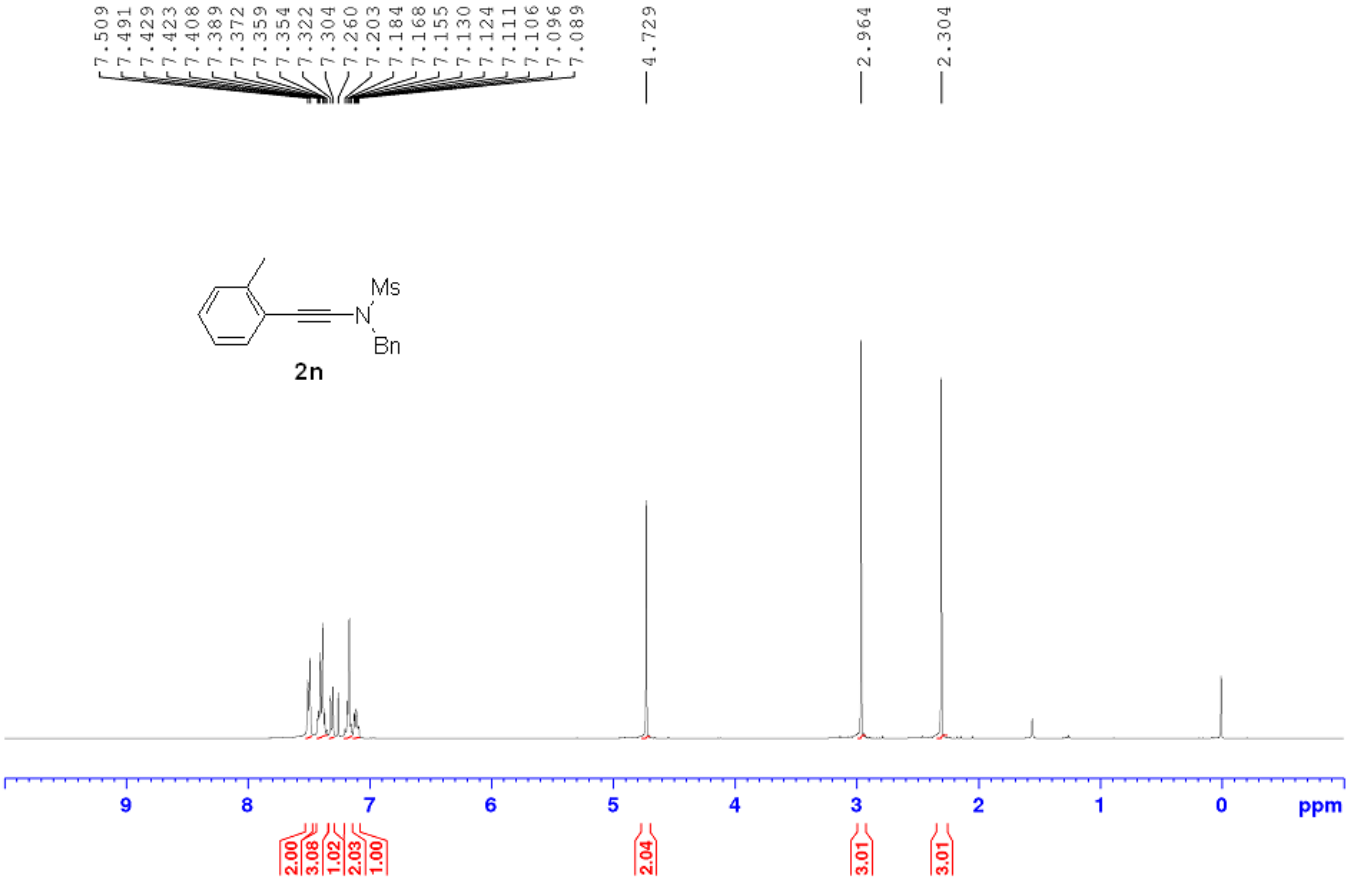


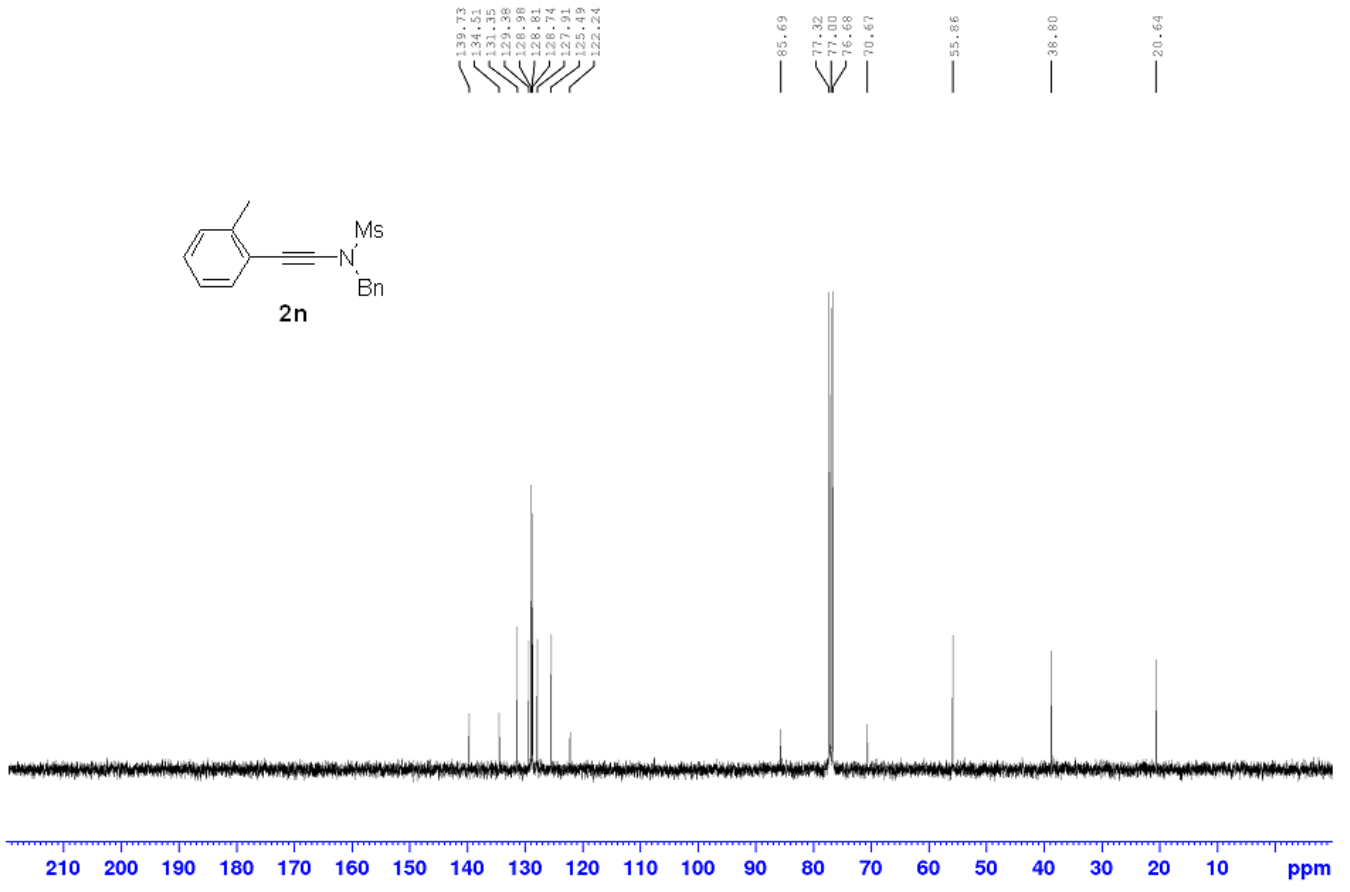
_N_-Benzyl-_N_-((3-nitrophenyl)ethynyl)methanesulfonamide (2m)



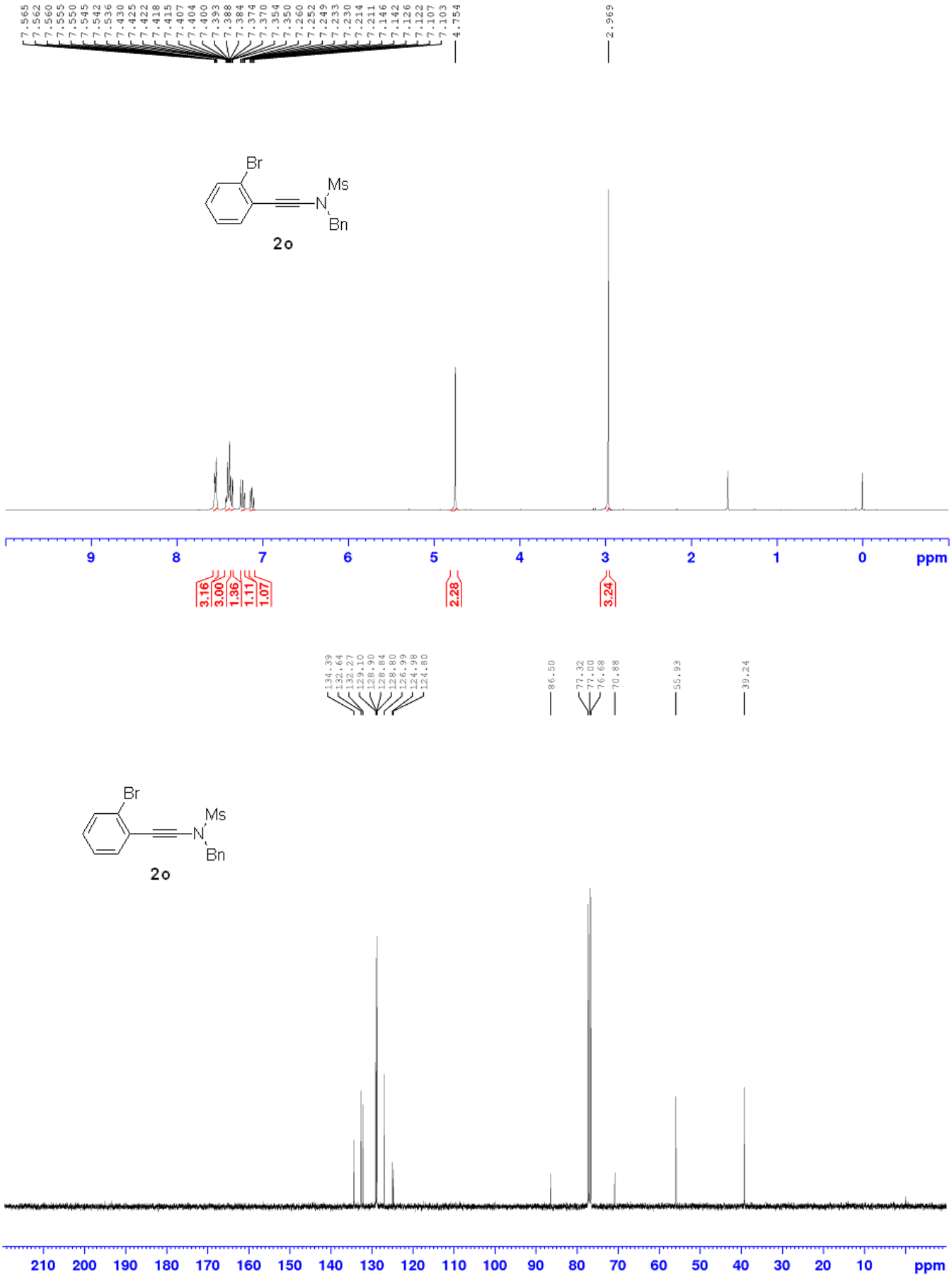


_N_-Benzyl-_N_-(_o_-tolylethynyl)methanesulfonamide (2n)

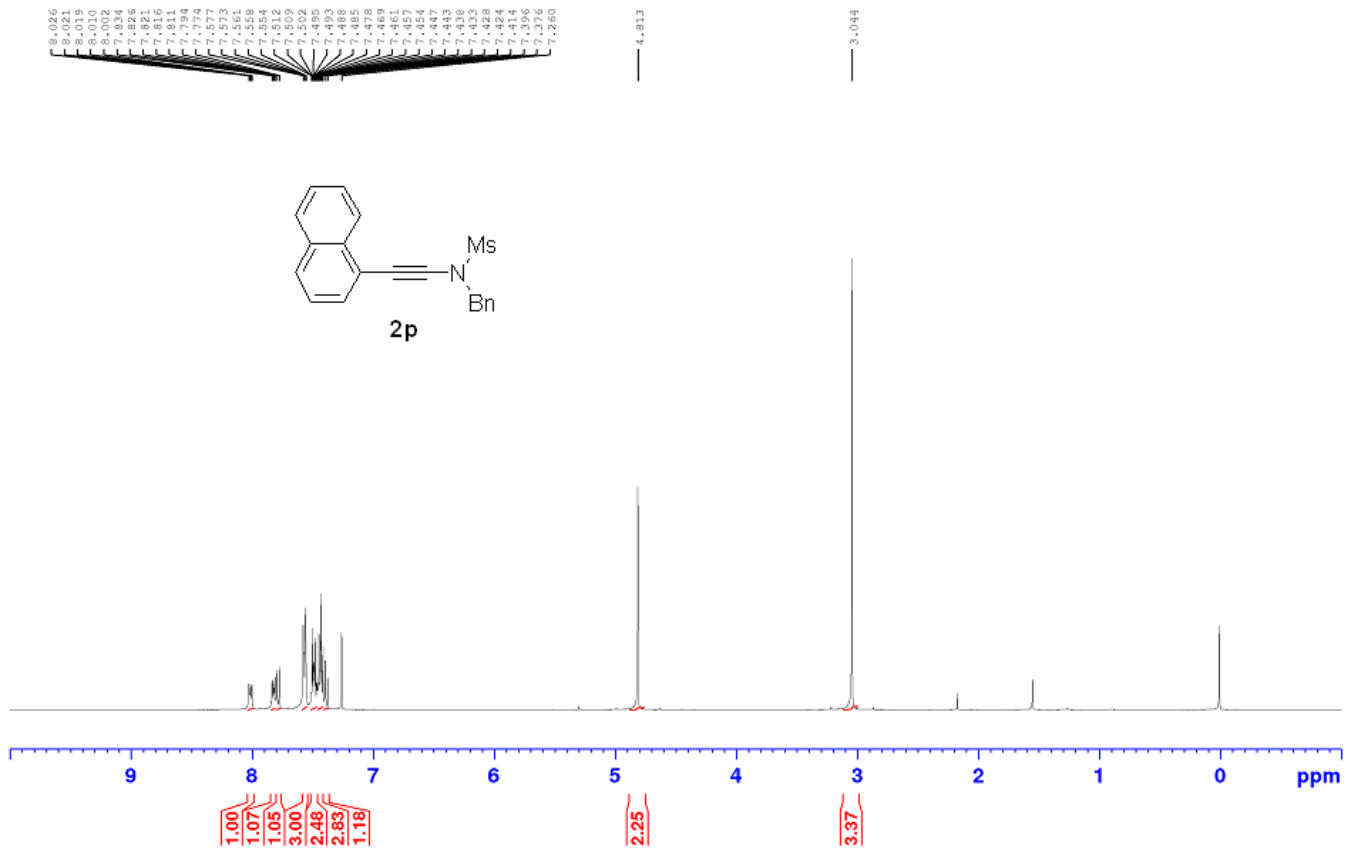


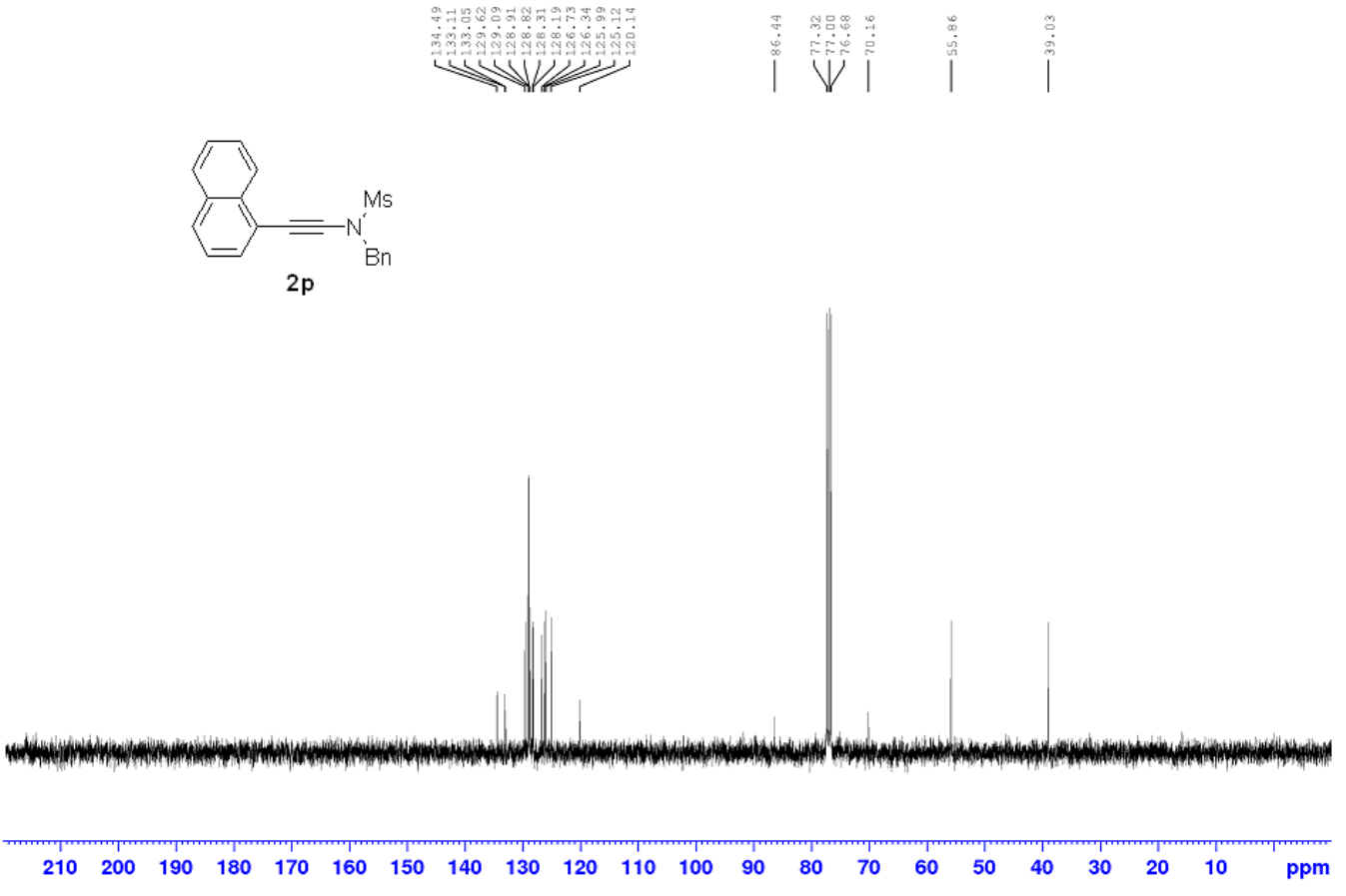


_N_-Benzyl-_N_-((2-bromophenyl)ethynyl)methanesulfonamide (2o)

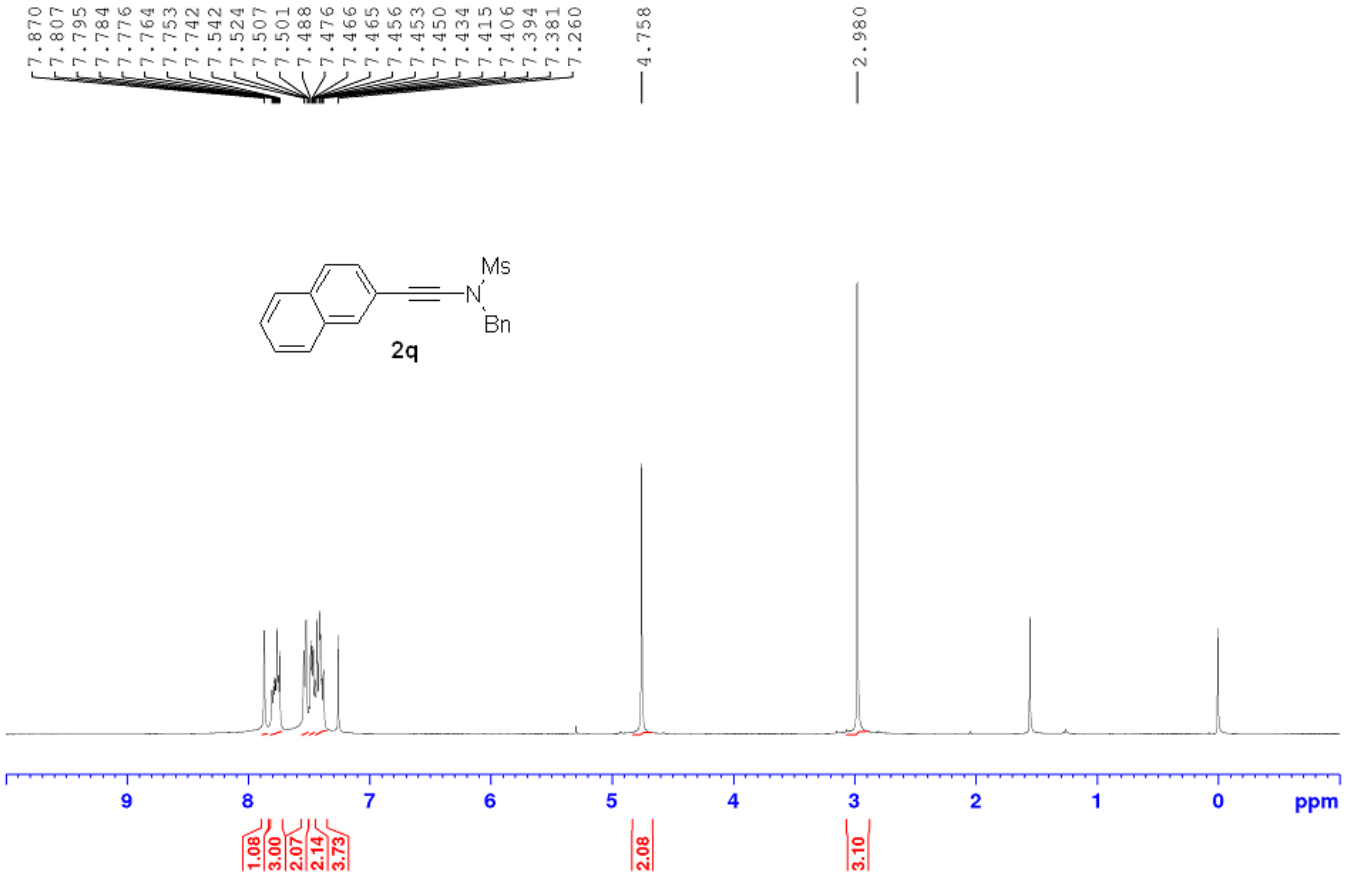


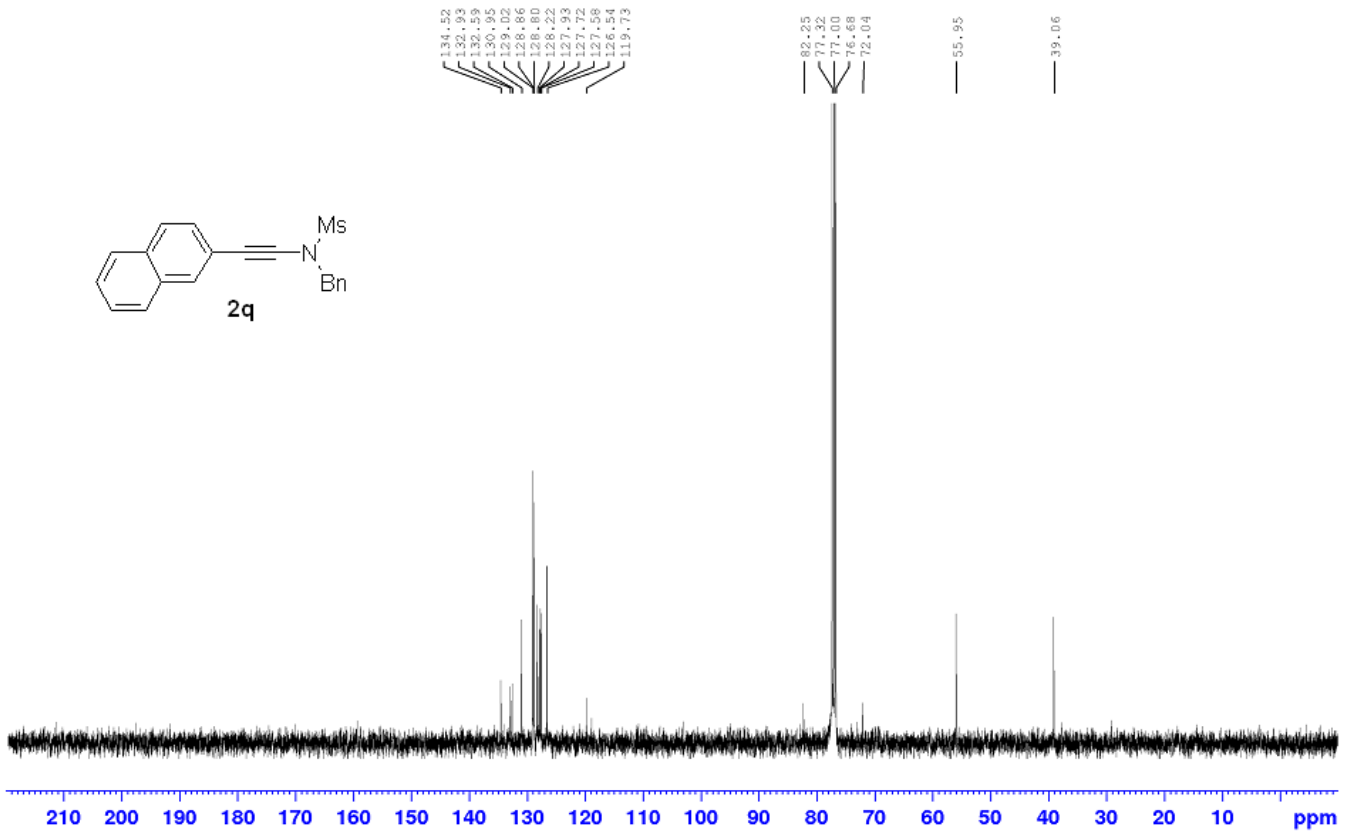
_N_-Benzyl-_N_-(naphthalen-1-ylethynyl)methanesulfonamide (2p)



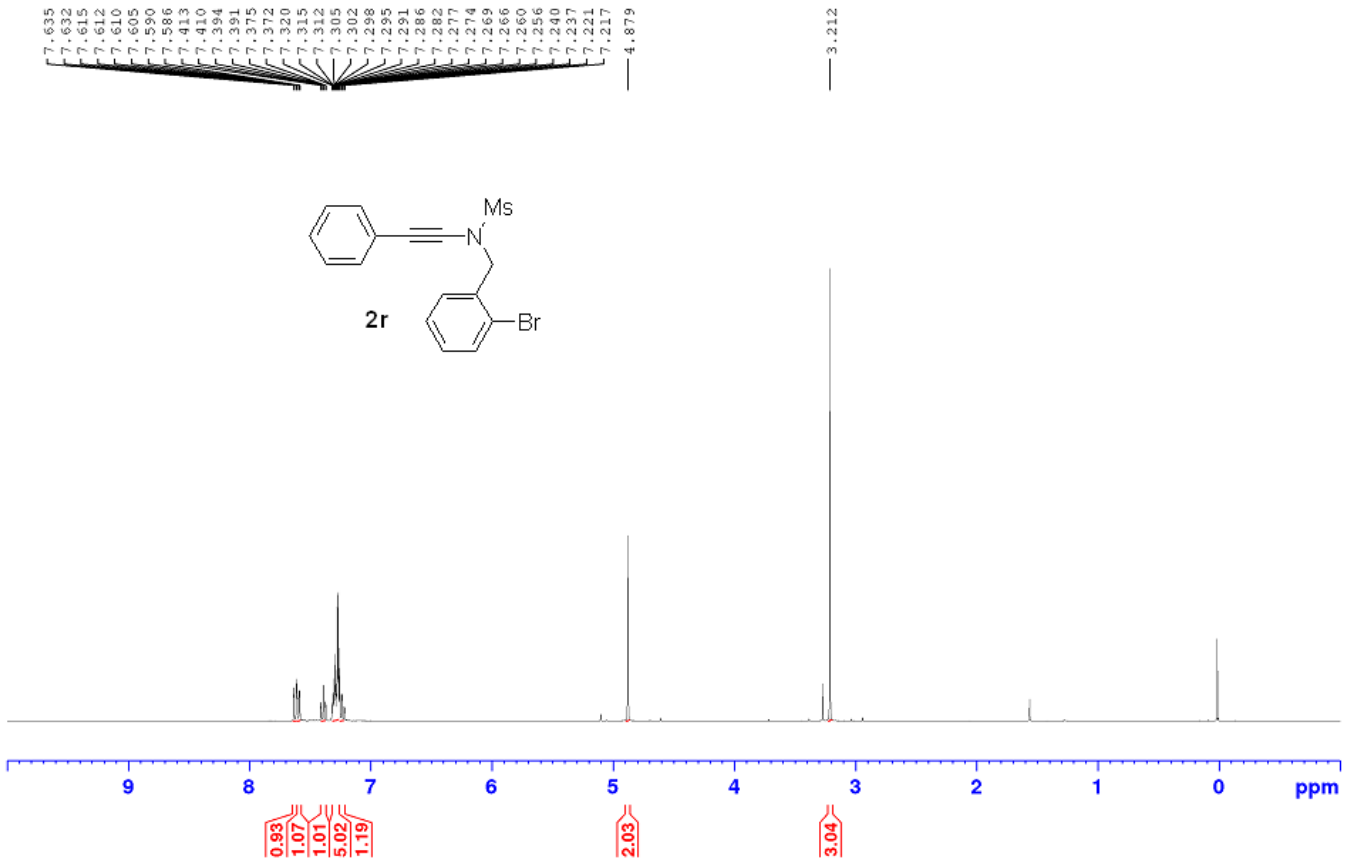


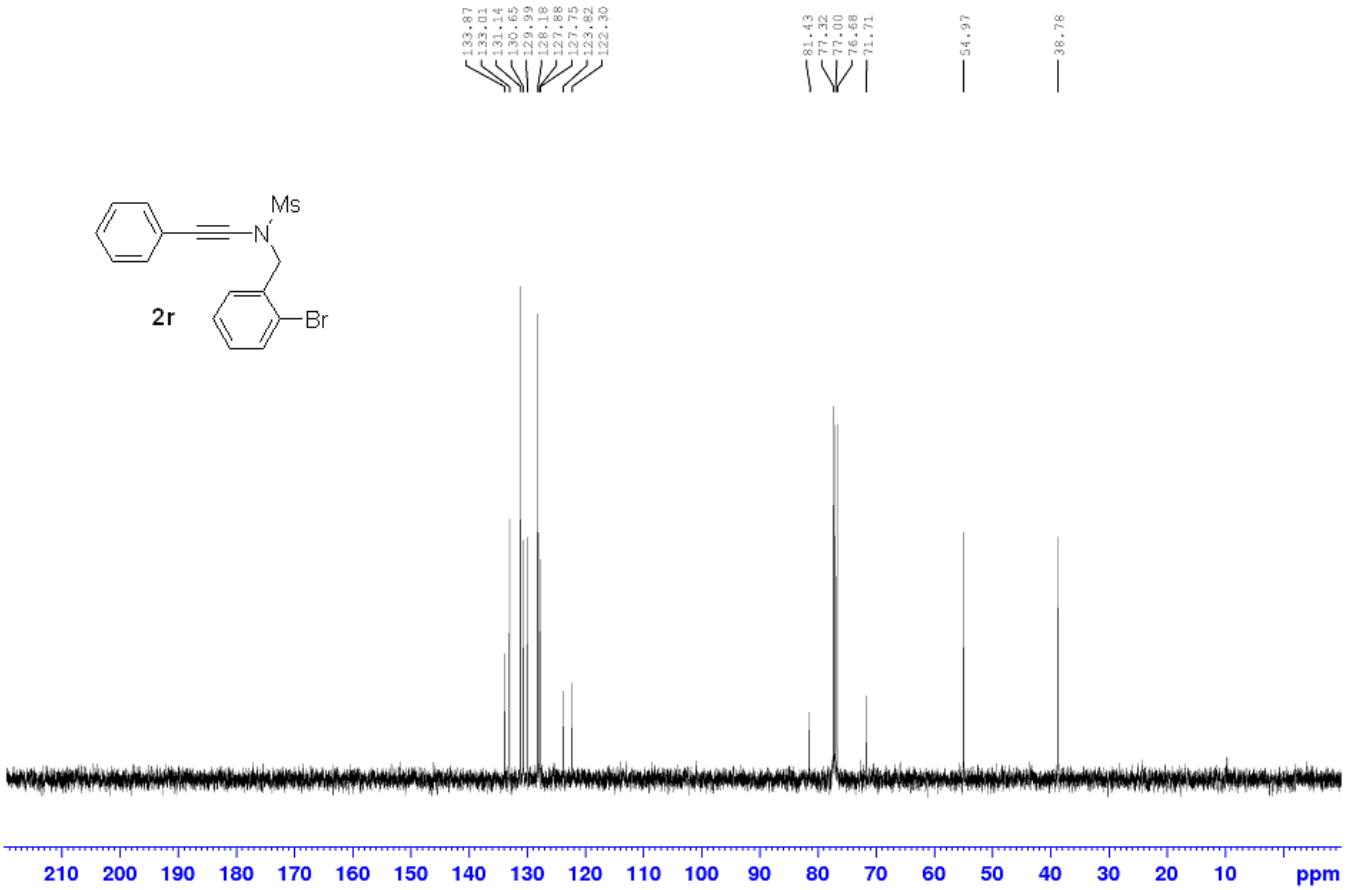
_N_-Benzyl-_N_-(naphthalen-2-ylethynyl)methanesulfonamide (2q)



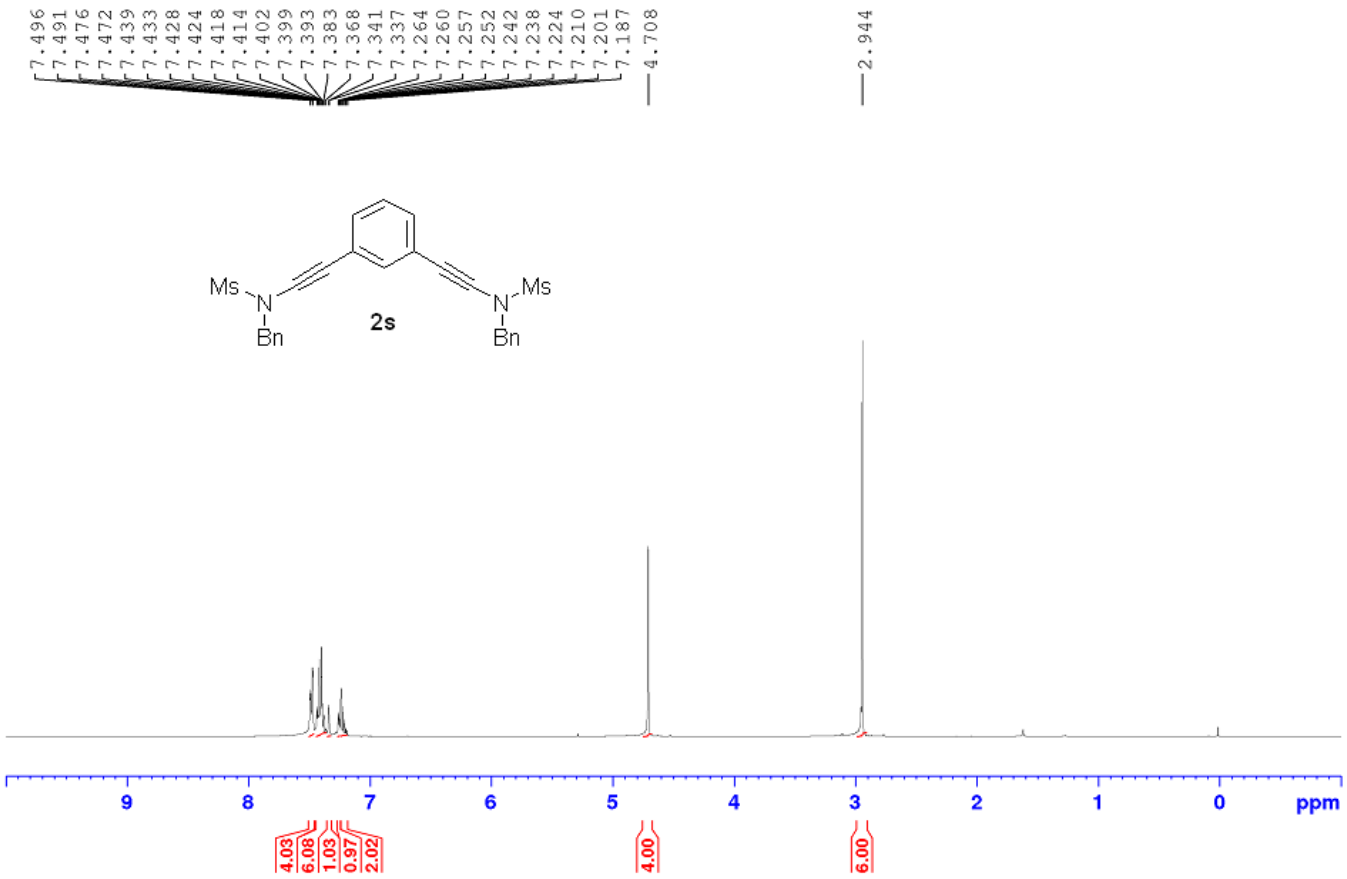


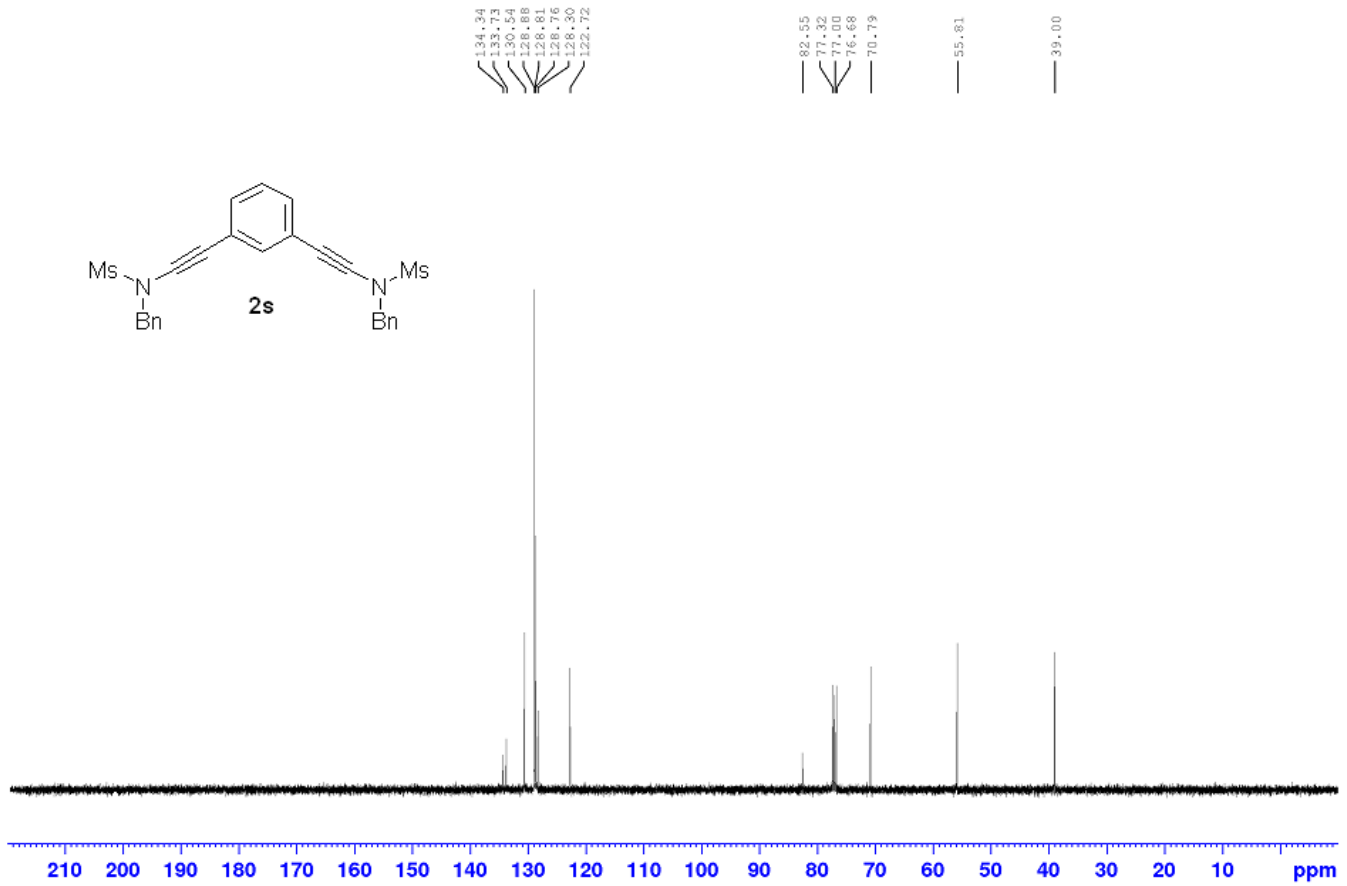
_N_-(2-Bromobenzyl)-_N_-(phenylethynyl)methanesulfonamide (2r)



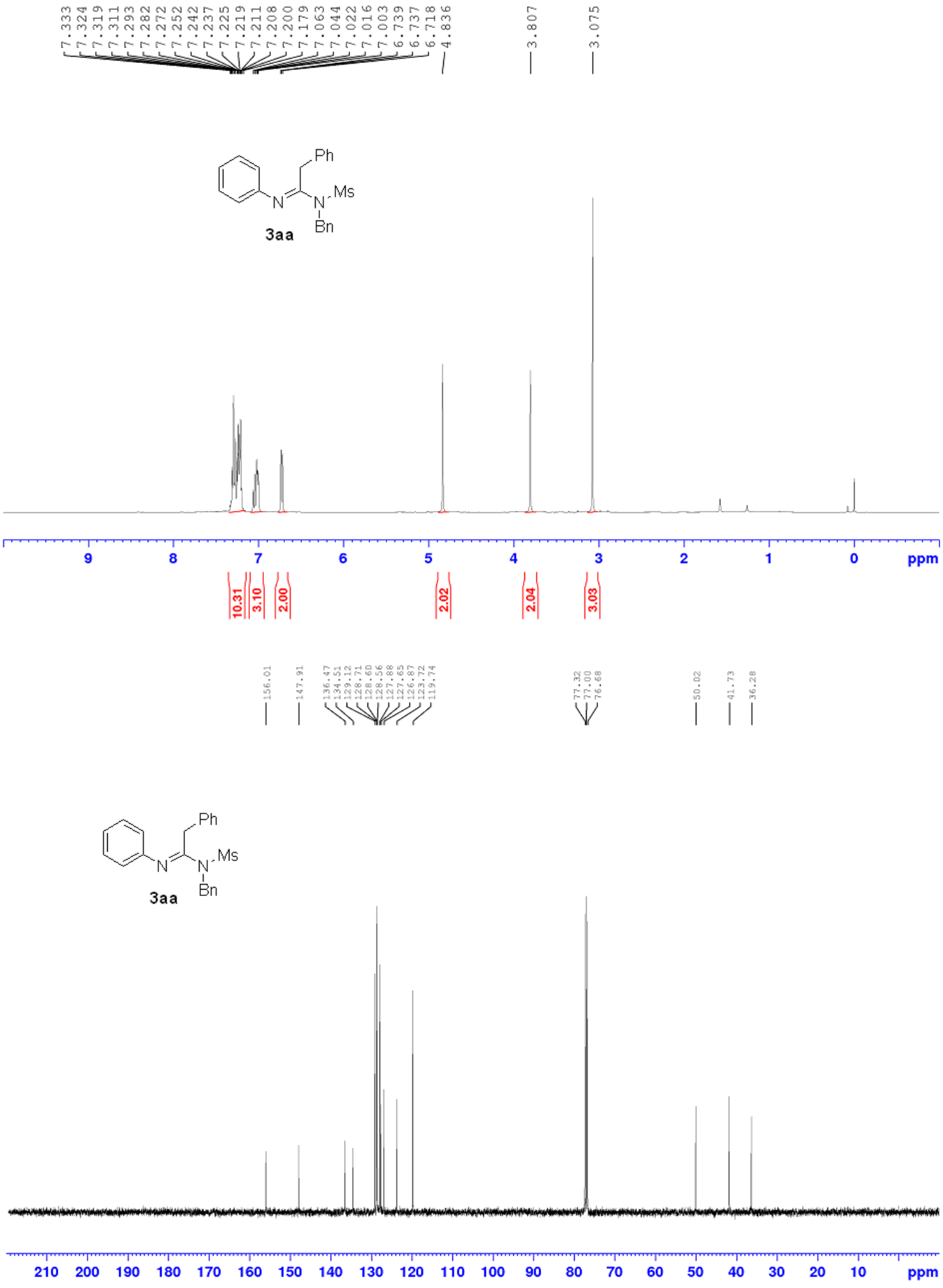


***N*,*N*′-(1,3-Phenylenebis(ethyne-2,1-diyl))bis(*N*-benzylmethanesulfonamide) (2s)**

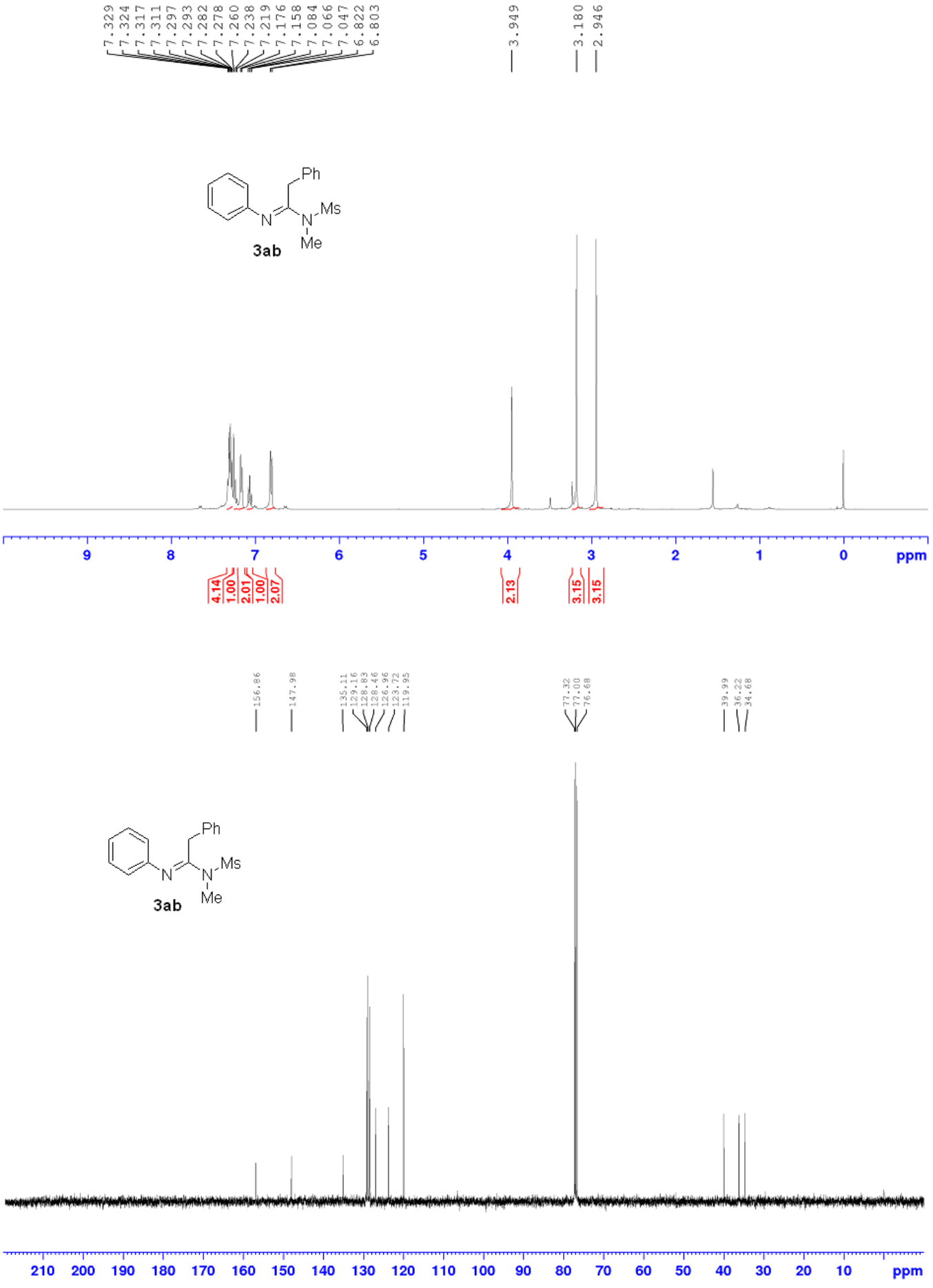




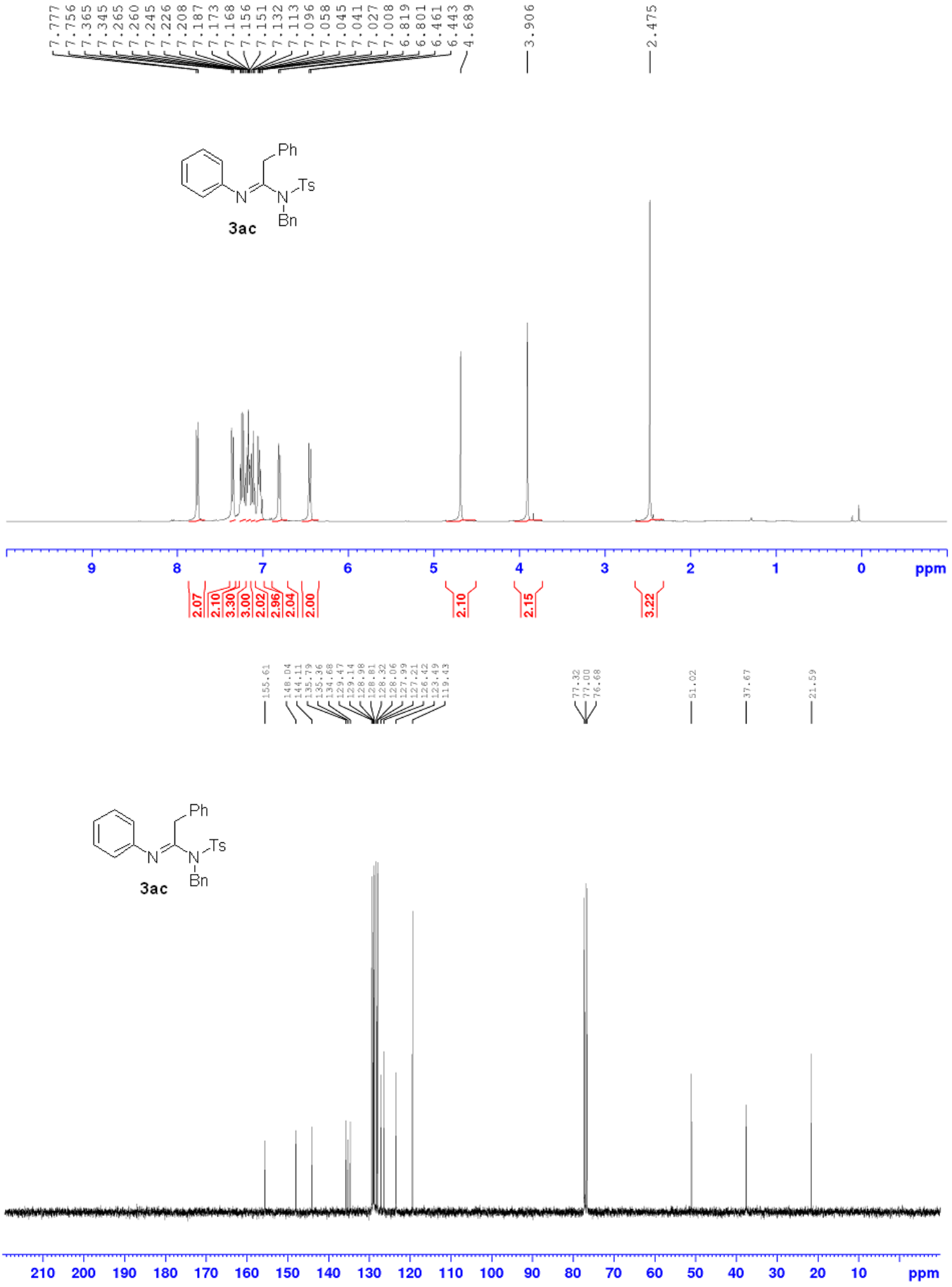
(*E*)-*N*-Benzyl-*N*-(methylsulfonyl)-*N*′,2-diphenylacetimidamide (3aa)



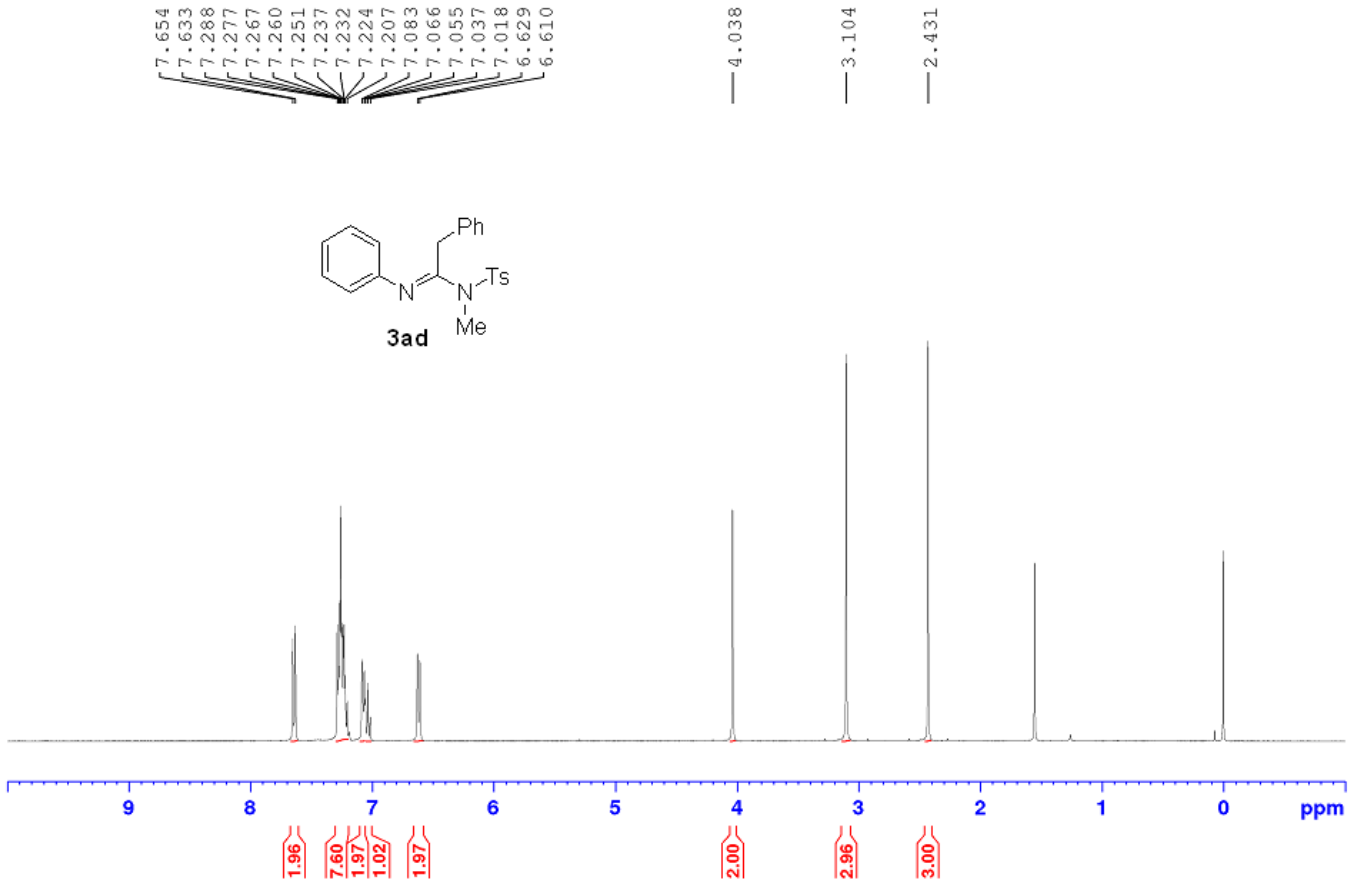
(*E*)-*N*-Methyl-*N*-(methylsulfonyl)-*N′*,2-diphenylacetimidamide (3ab)

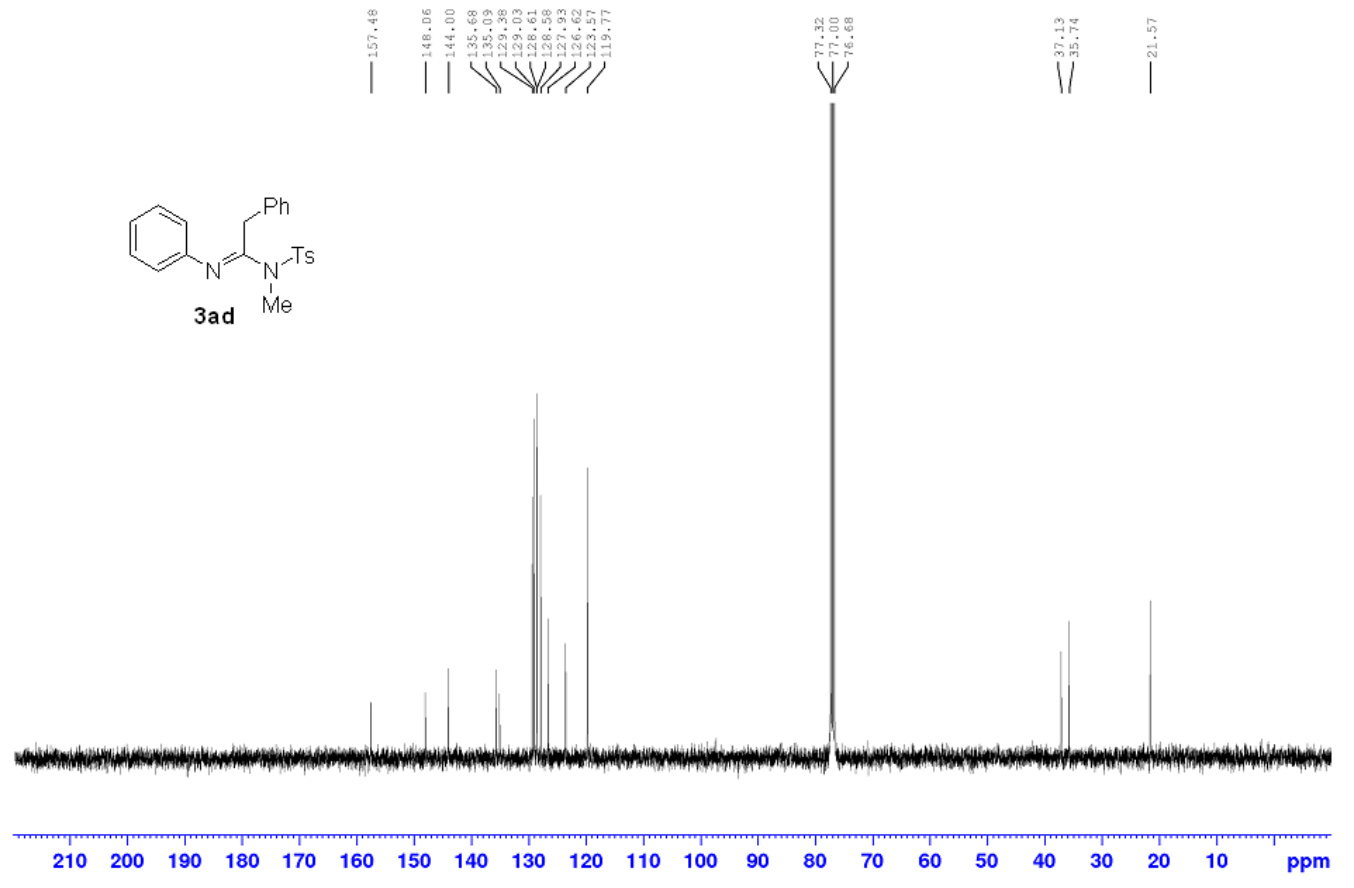


(*E*)-*N*-Benzyl-*N*′,2-diphenyl-*N*-tosylacetimidamide (3ac)

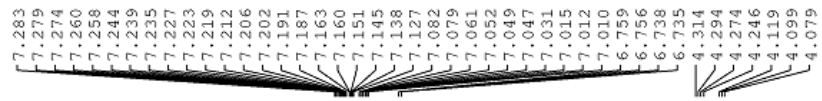


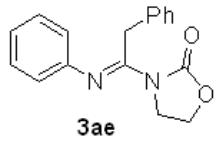
(*E*)-*N*-Methyl-*N*′,2-diphenyl-*N*-tosylacetimidamide (3ad)



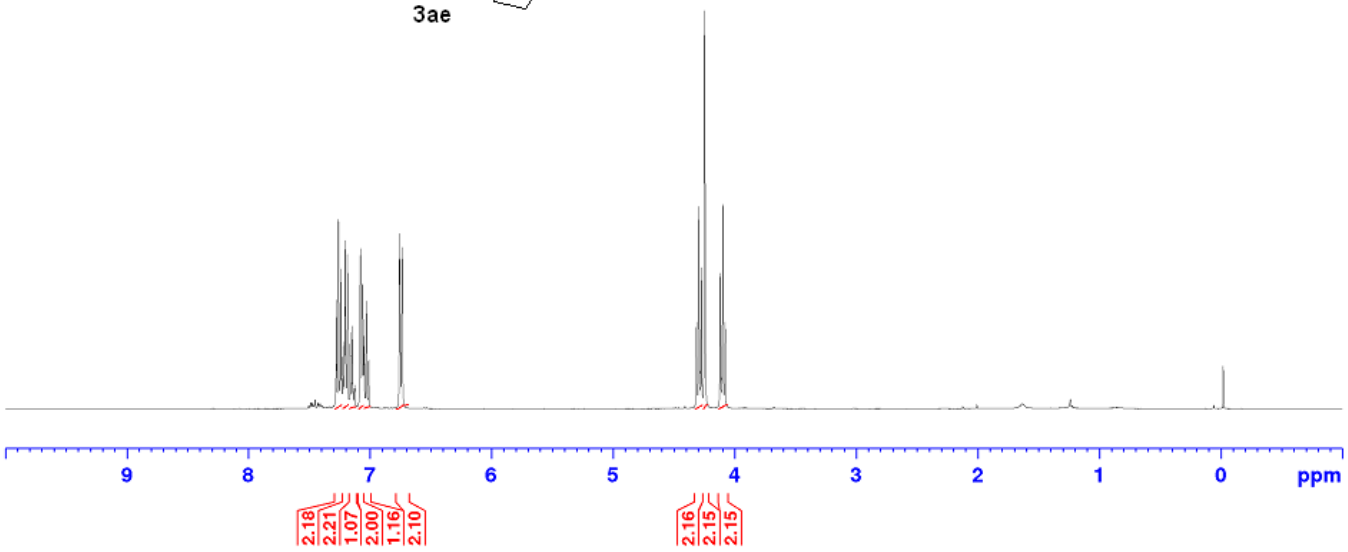


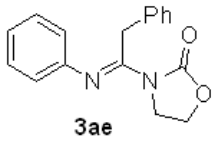
(*E*)-3-(2-Phenyl-1-(phenylimino)ethyl)oxazolidin-2-one (3ae)





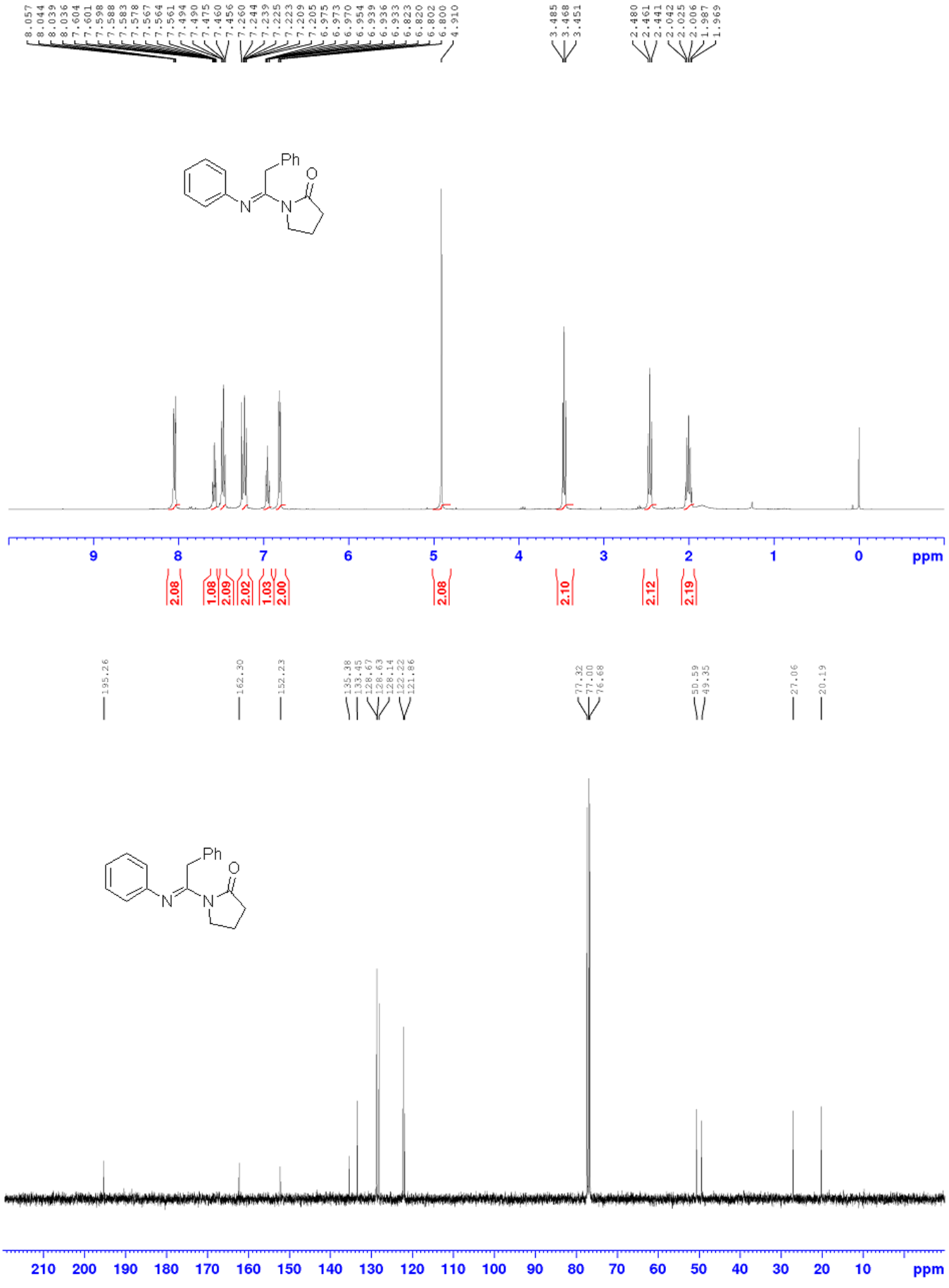
3ae



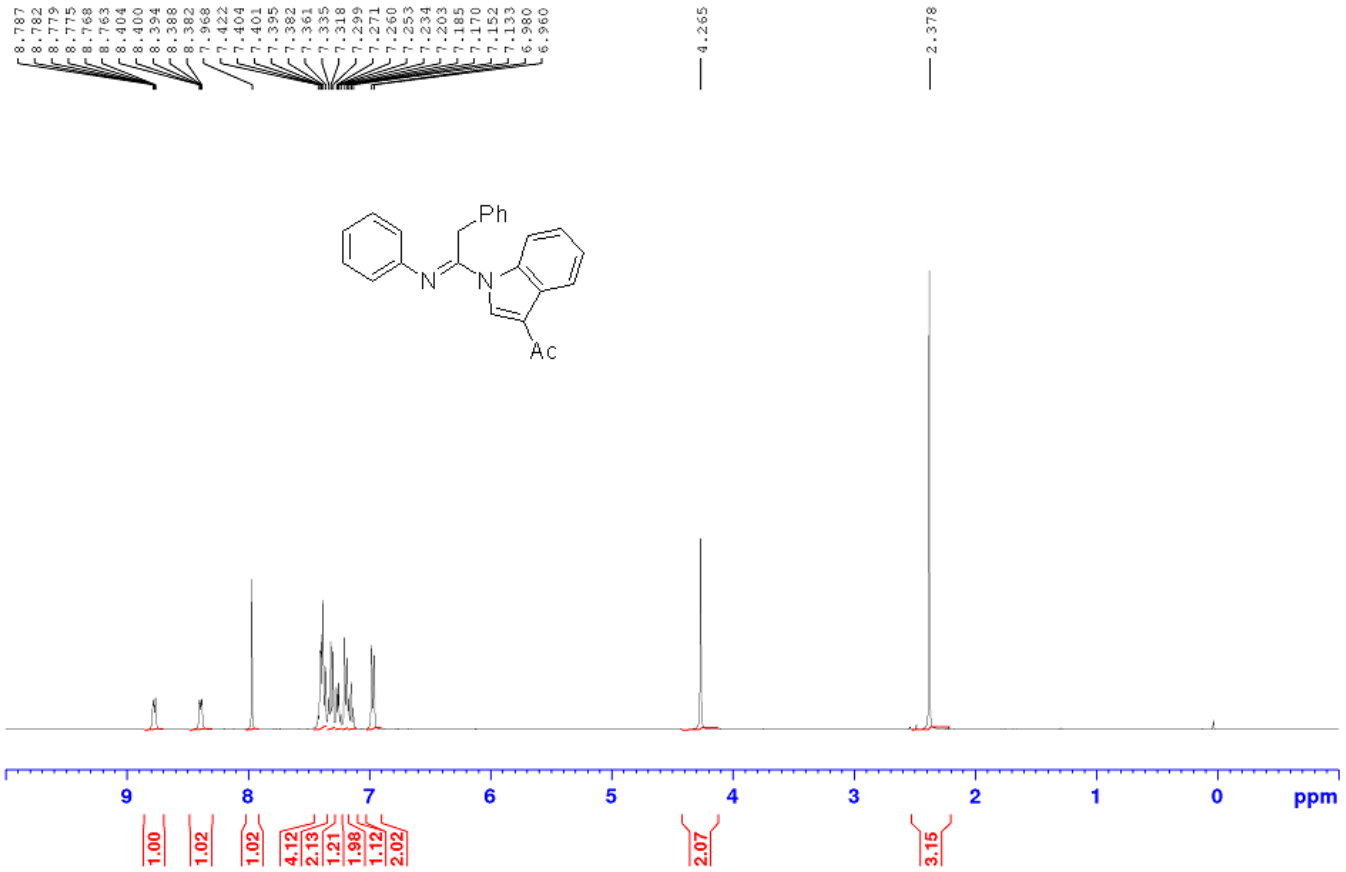


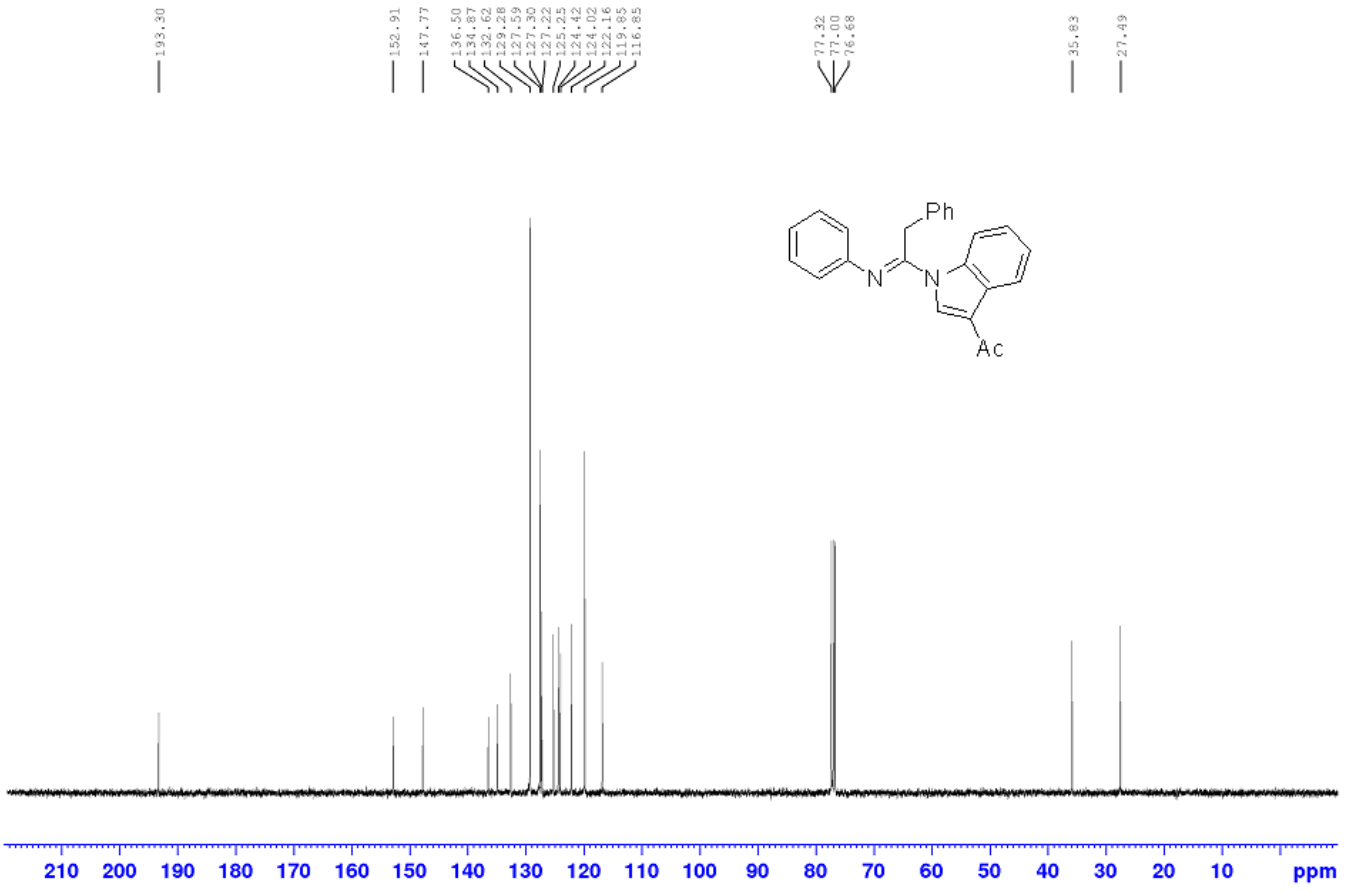
3ae

(*E*)-1-(2-Phenyl-1-(phenylimino)ethyl)pyrrolidin-2-one

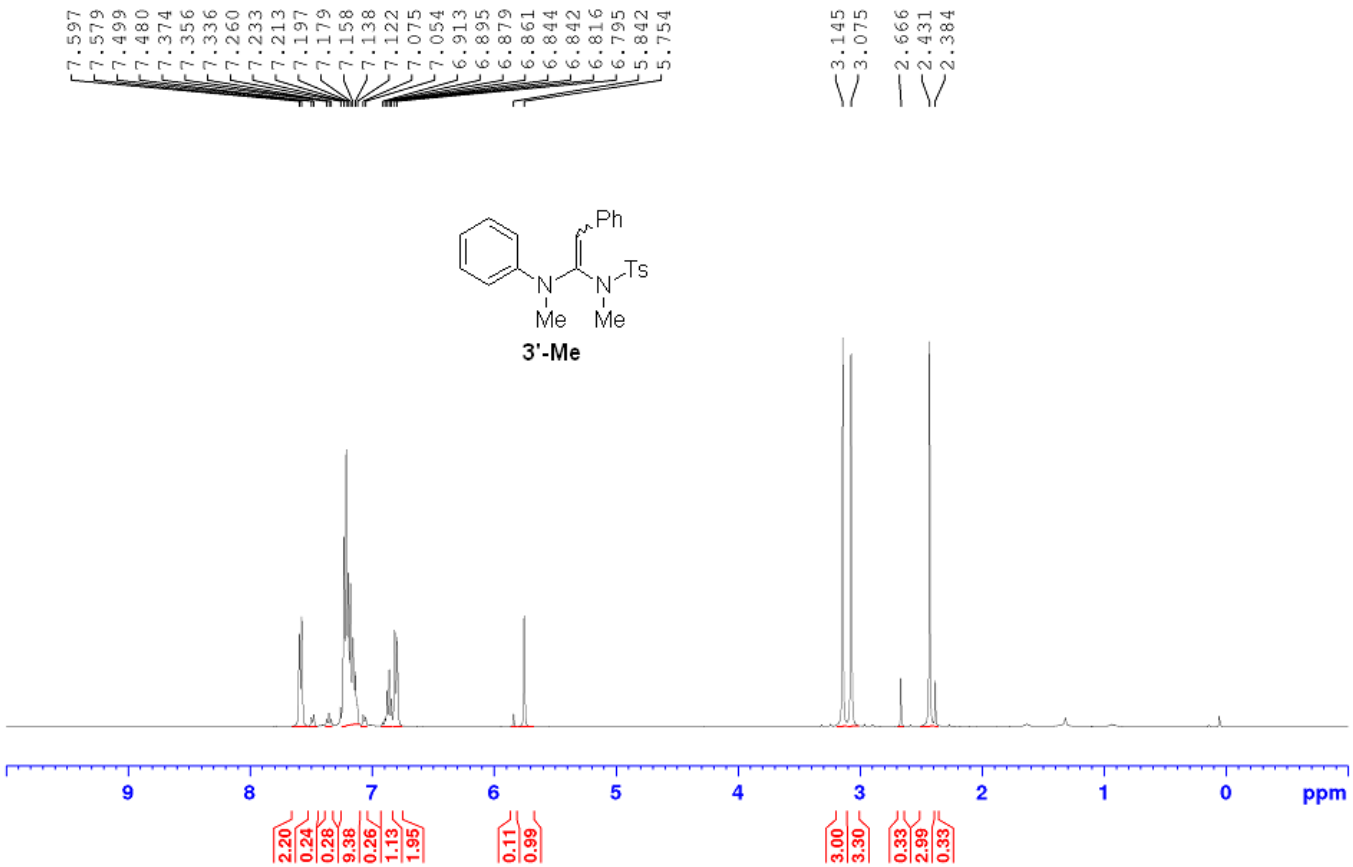


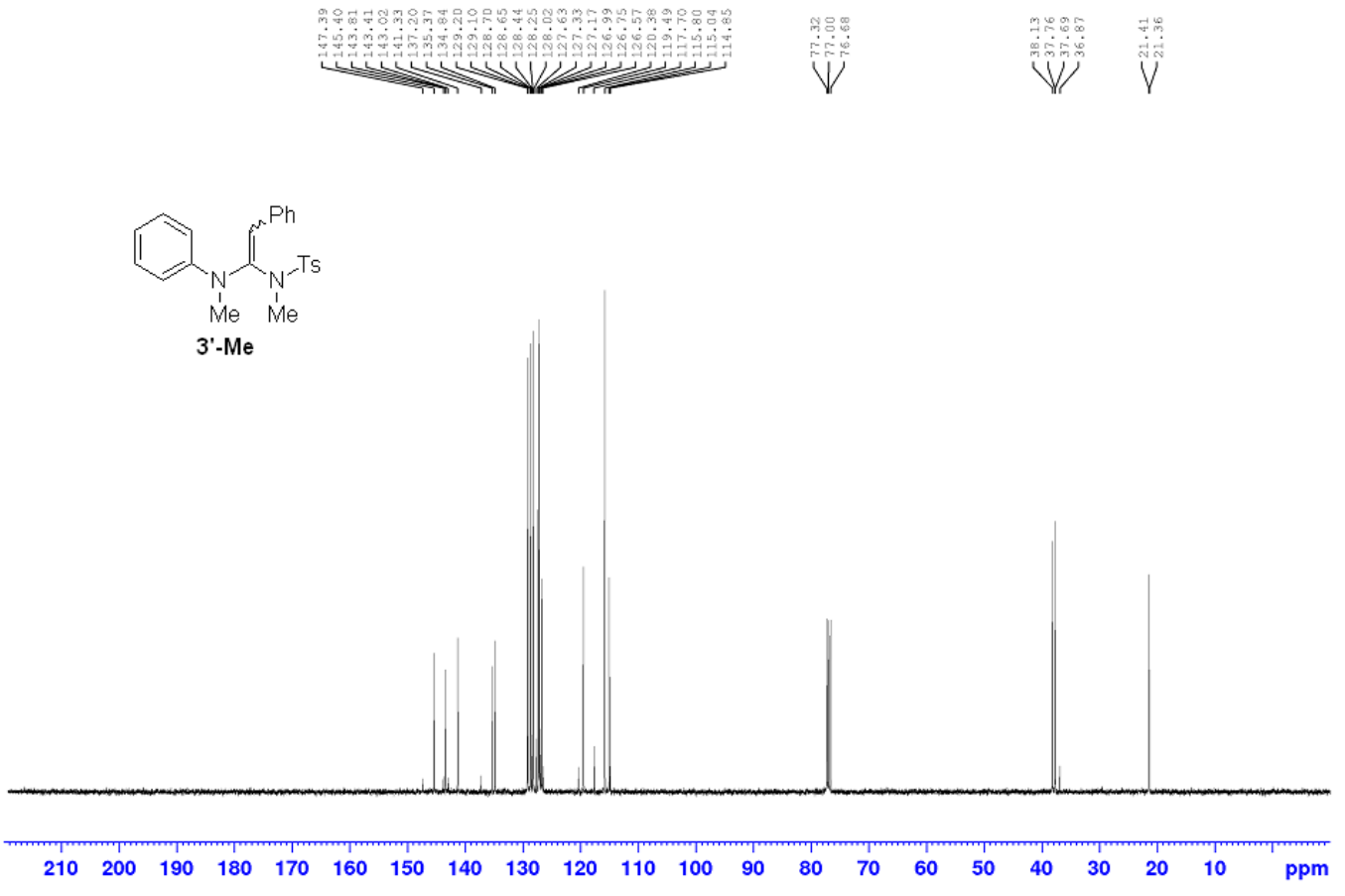
(*E*)-1-(1-(2-Phenyl-1-(phenylimino)ethyl)-1*H*-indol-3-yl)ethan-1-one



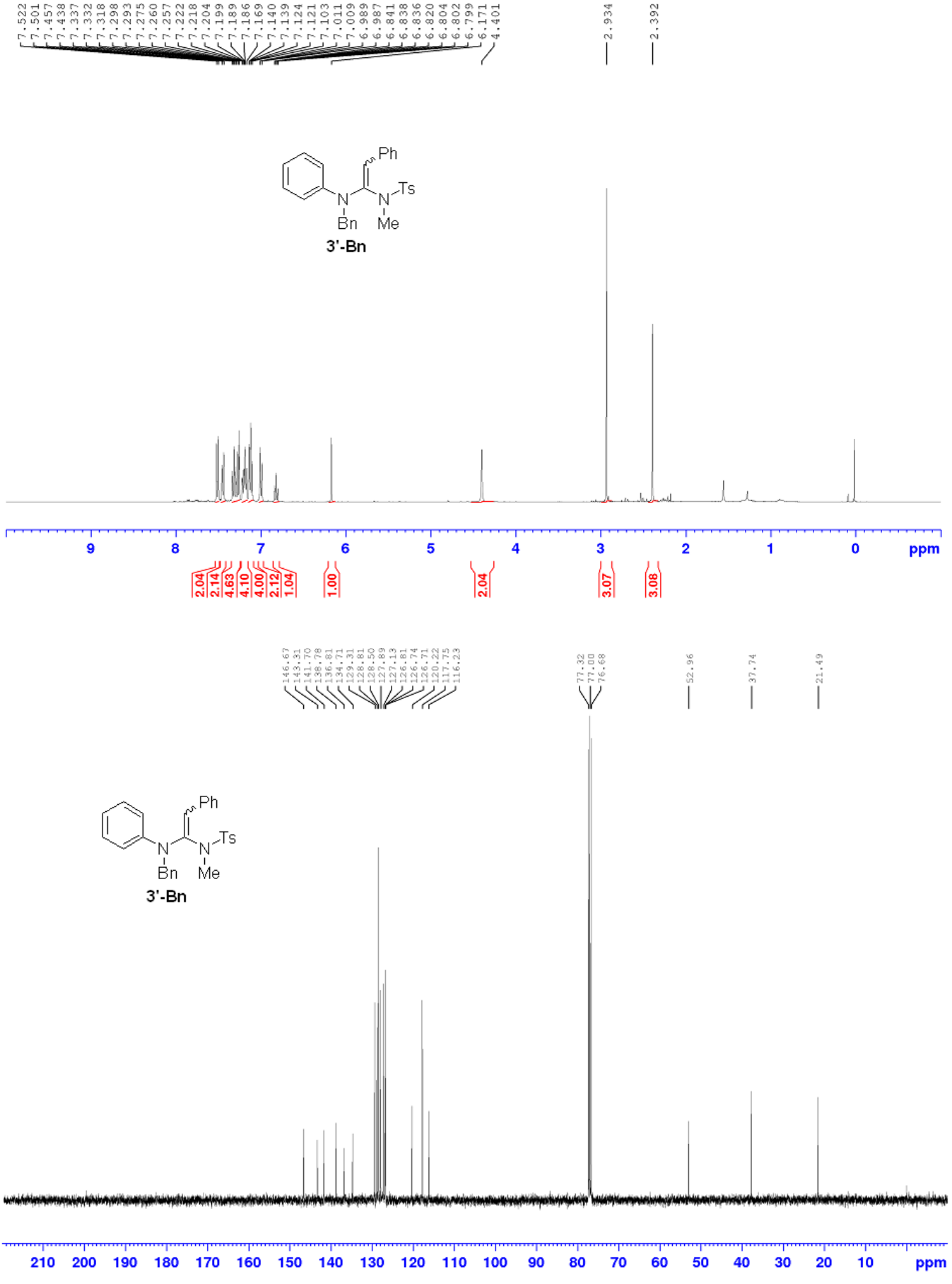


_N_,4-Dimethyl-_N_-(1-(methyl(phenyl)amino)-2-phenylvinyl)benzenesulfonamide (3′-Me)

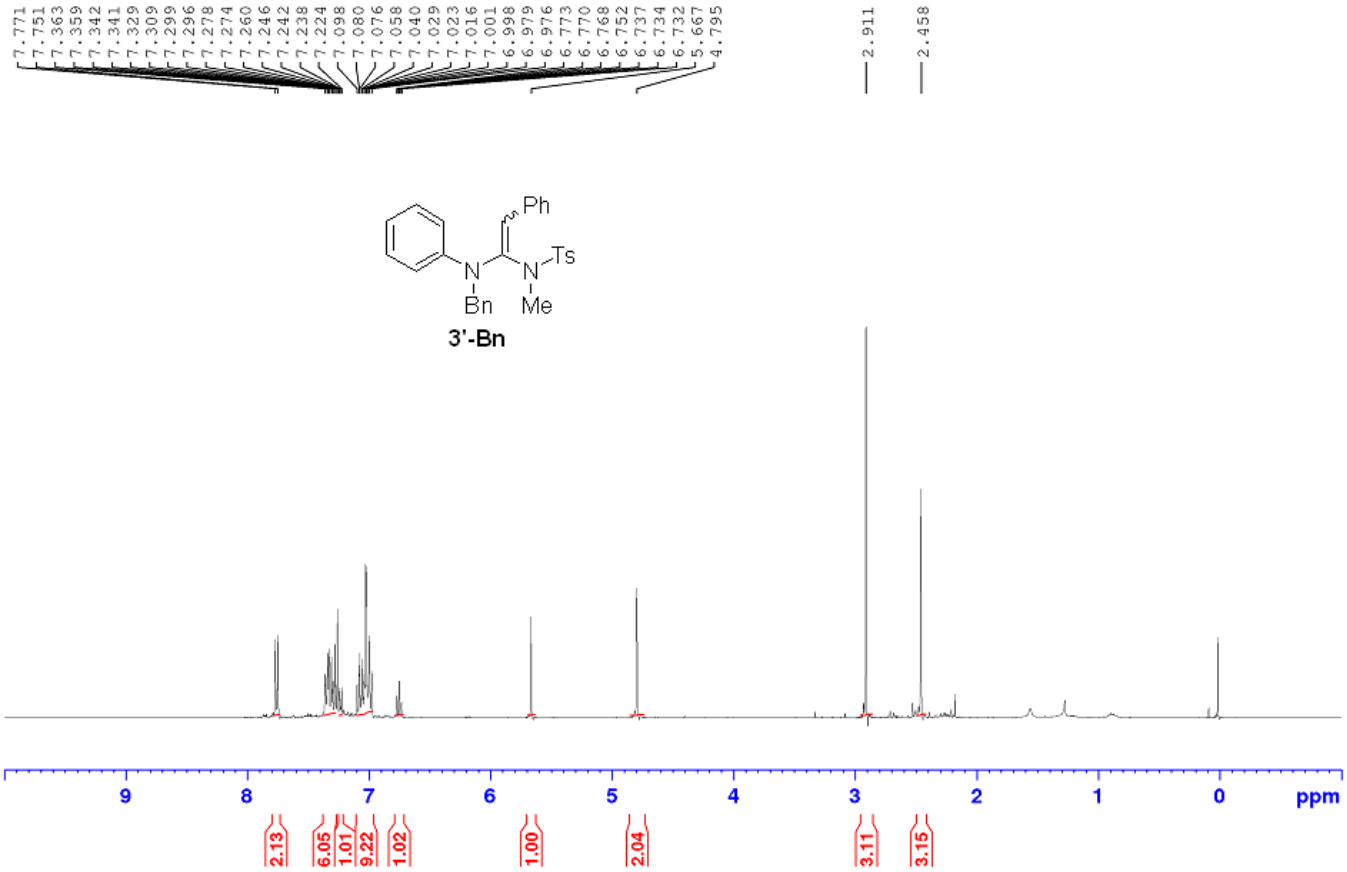


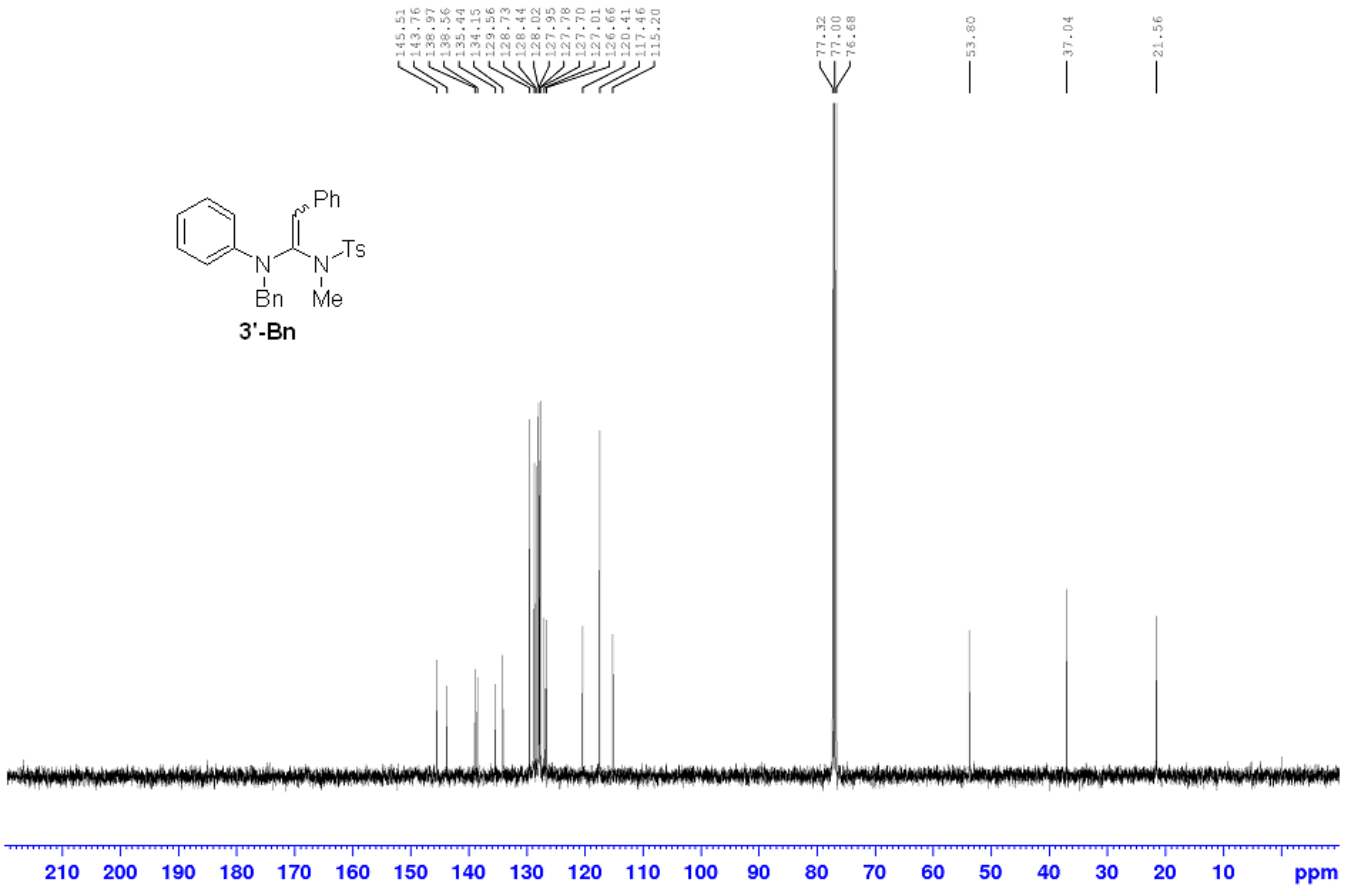


_N_-(1-(Benzyl(phenyl)amino)-2-phenylvinyl)-_N_,4-dimethylbenzenesulfonamide (3′-Bn) - A

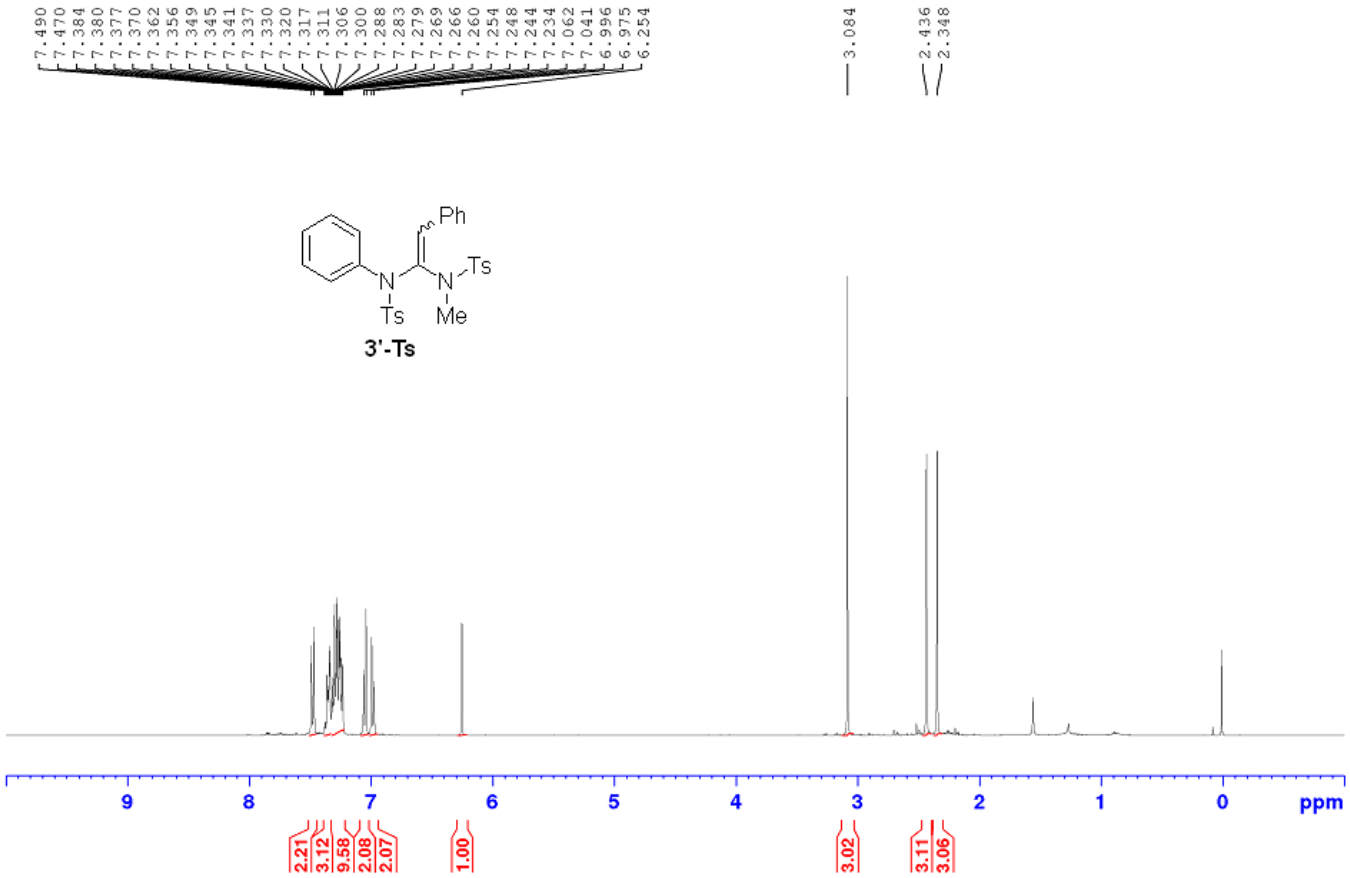


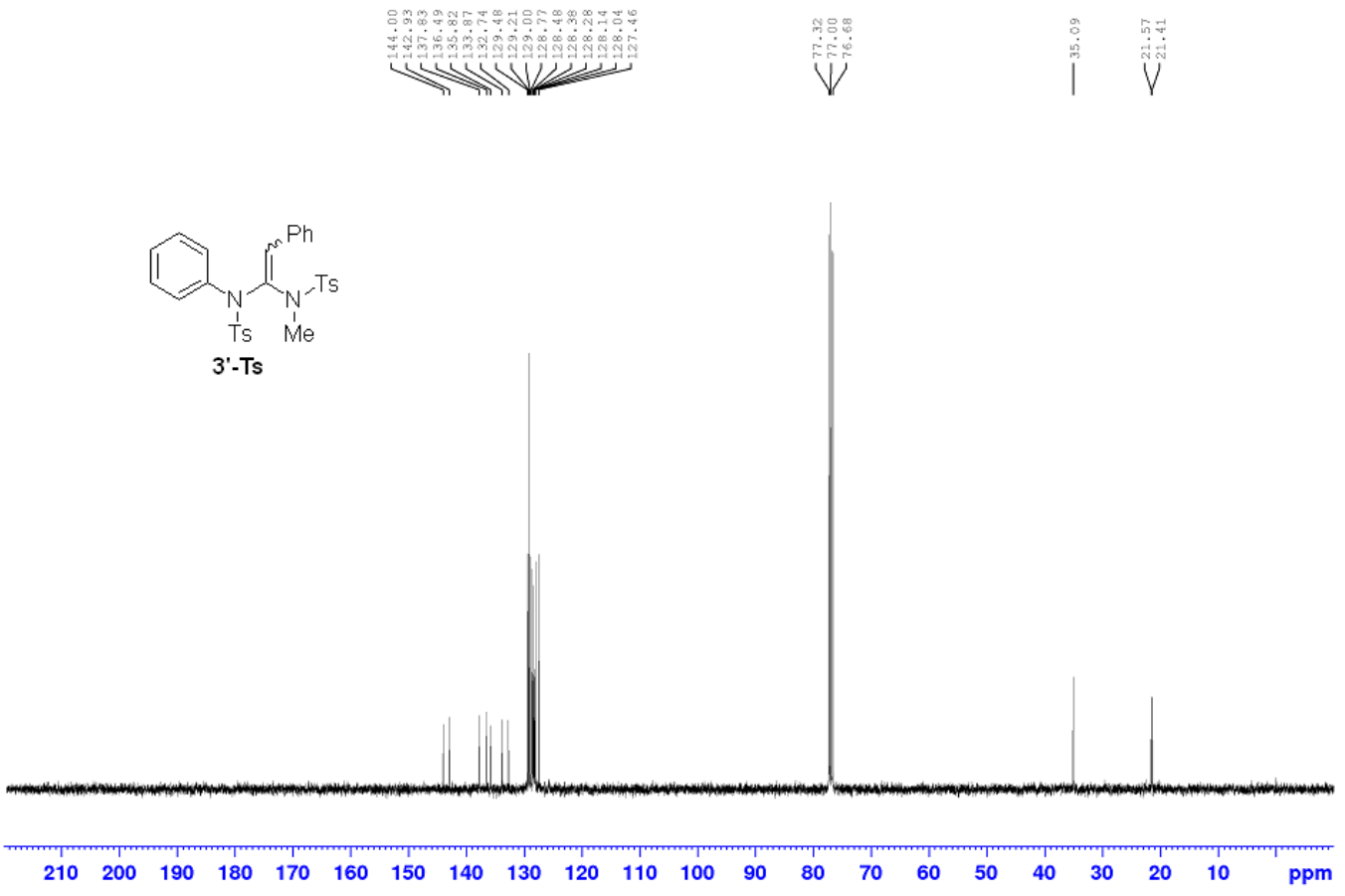
***N*-(1-(Benzyl(phenyl)amino)-2-phenylvinyl)-*N*,4-dimethylbenzenesulfonamide (3′-Bn) - B**



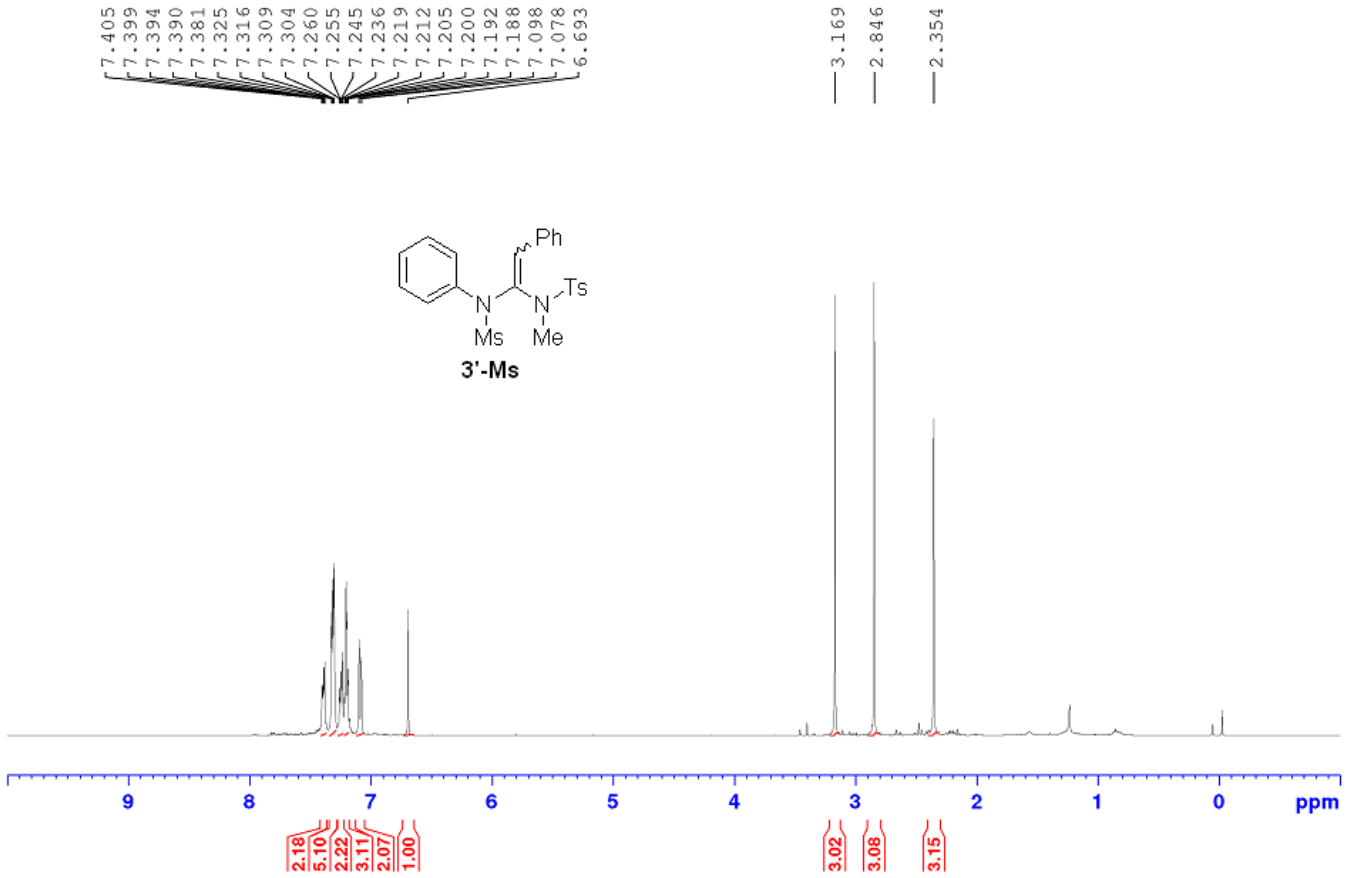


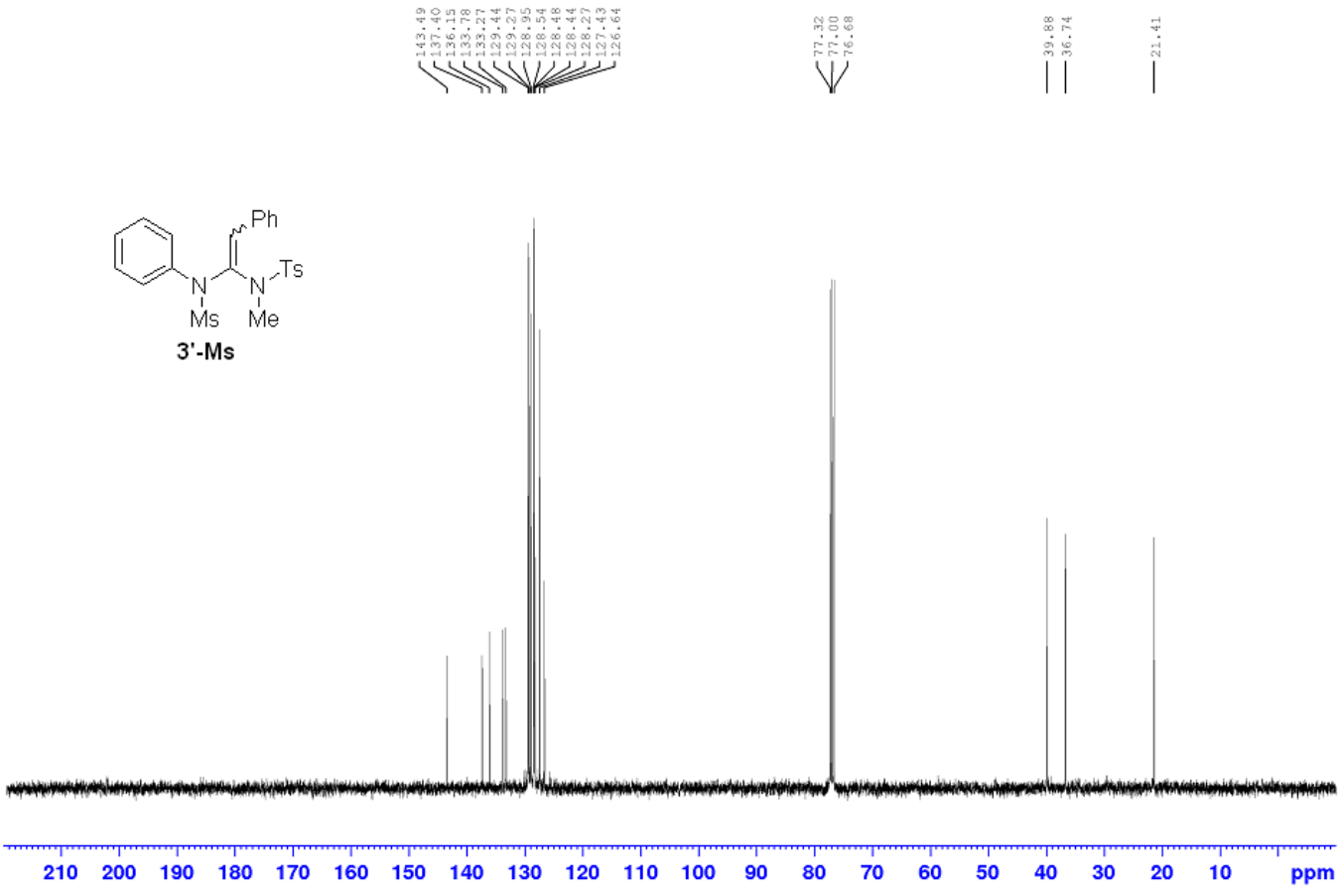
***N*-(1-((*N*,4-Dimethylphenyl)sulfonamido)-2-phenylvinyl)-4-methyl-*N*-phenylbenzenesulfonamide (3′-Ts)**



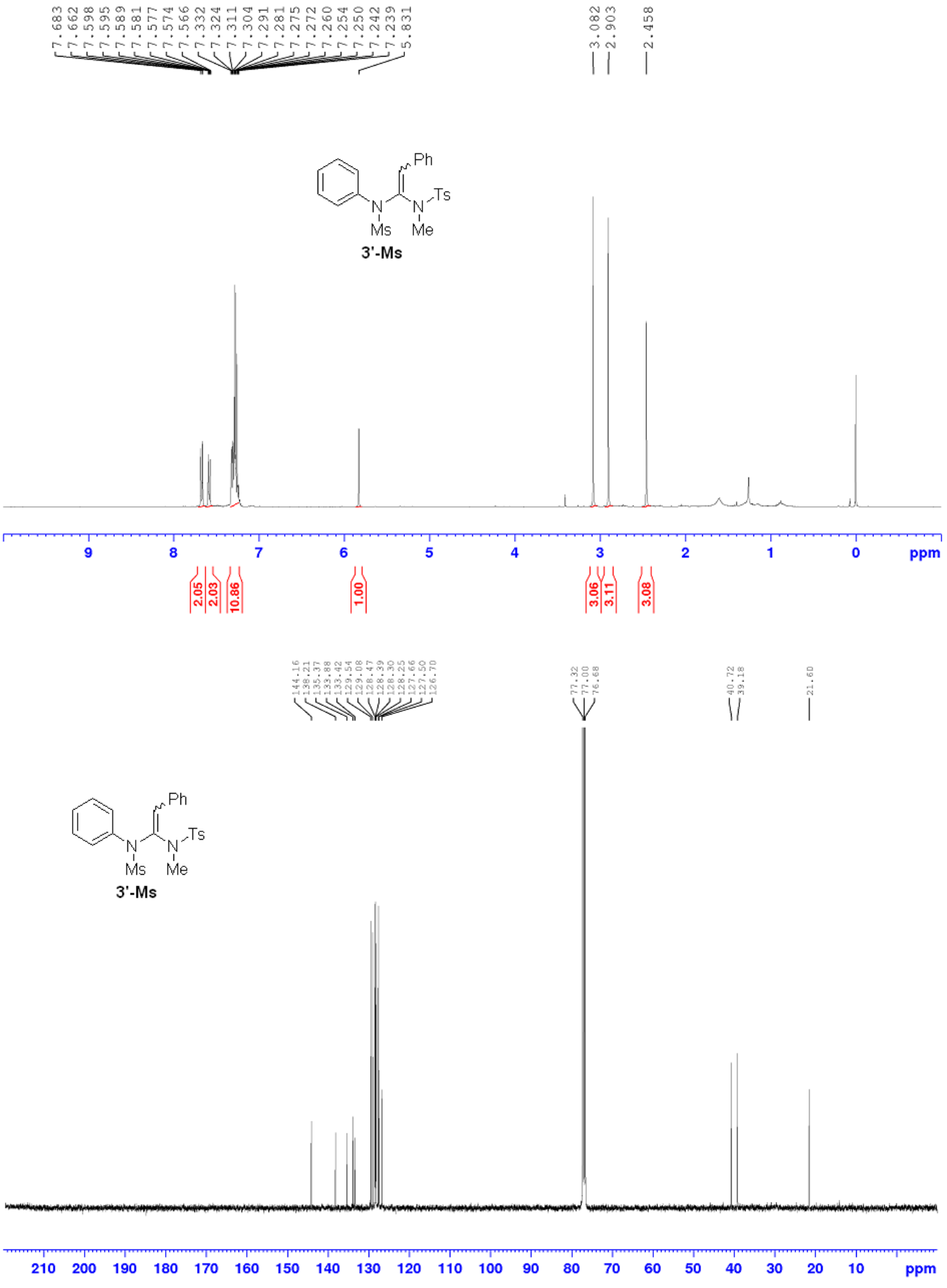


_N_,4-Dimethyl-_N_-(2-phenyl-1-(_N_-phenylmethylsulfonamido)vinyl)benzenesulfonamide (3′-Ms) - A

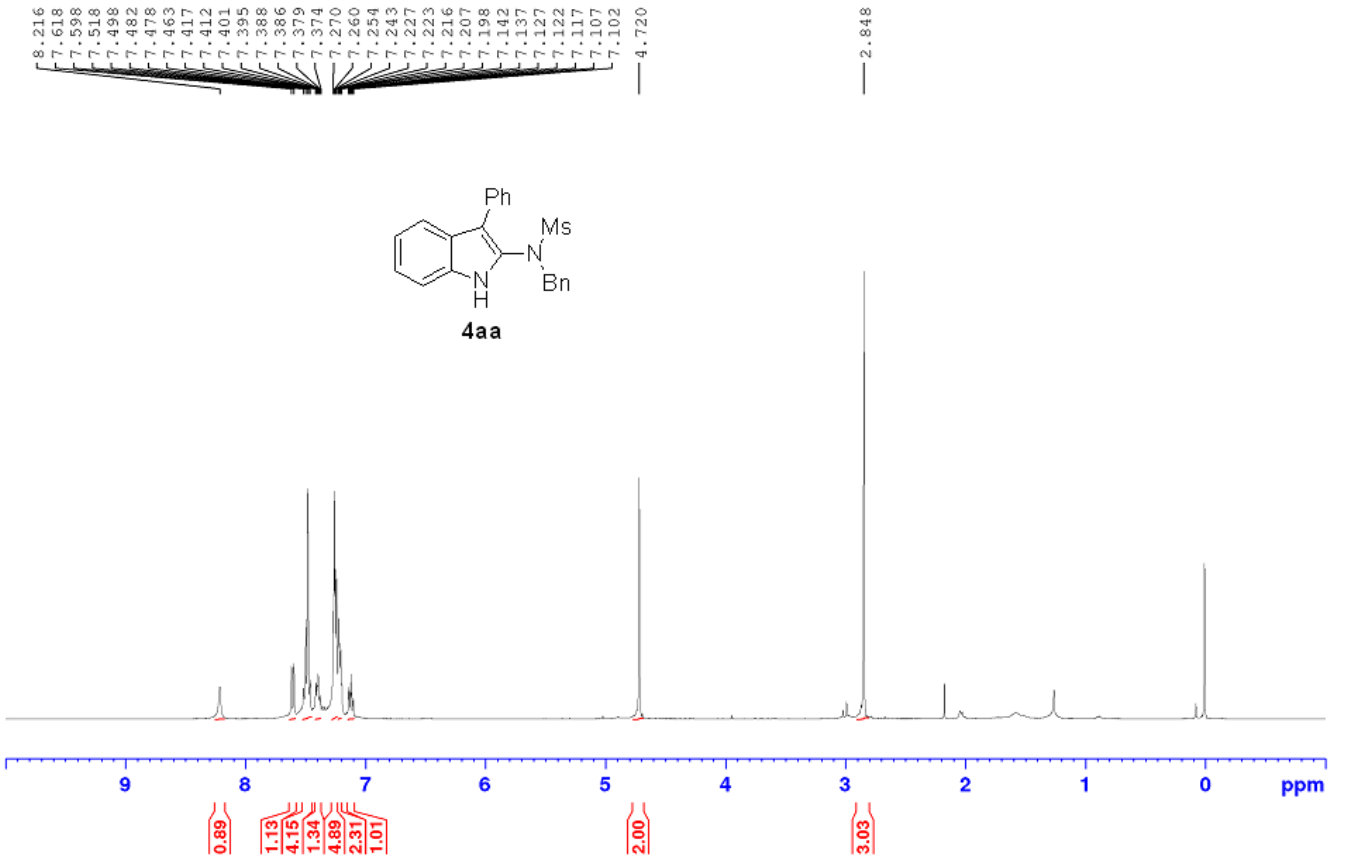


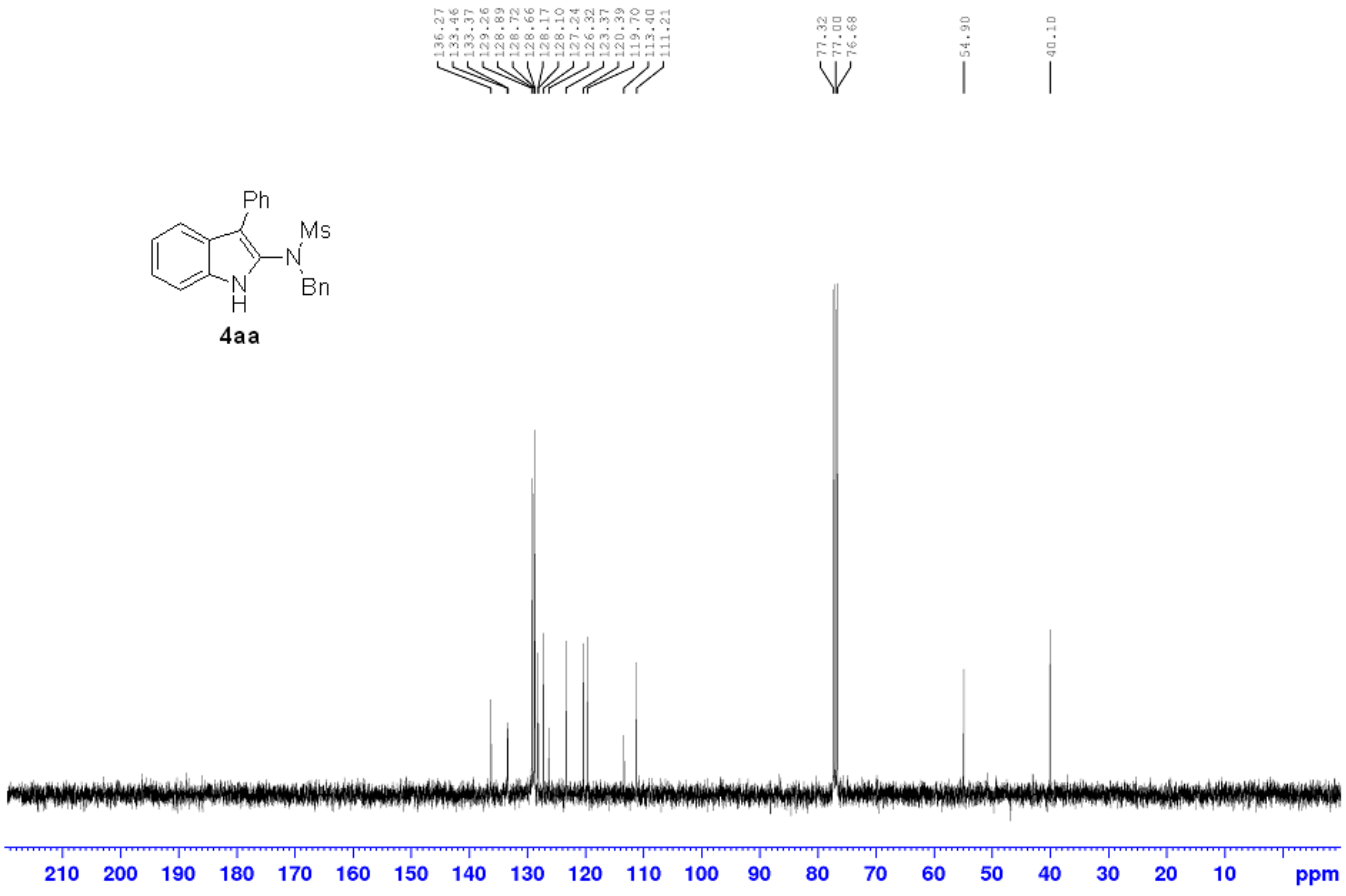


_N_,4-Dimethyl-_N_-(2-phenyl-1-(_N_-phenylmethylsulfonamido)vinyl)benzenesulfonamide (3′-Ms) - B

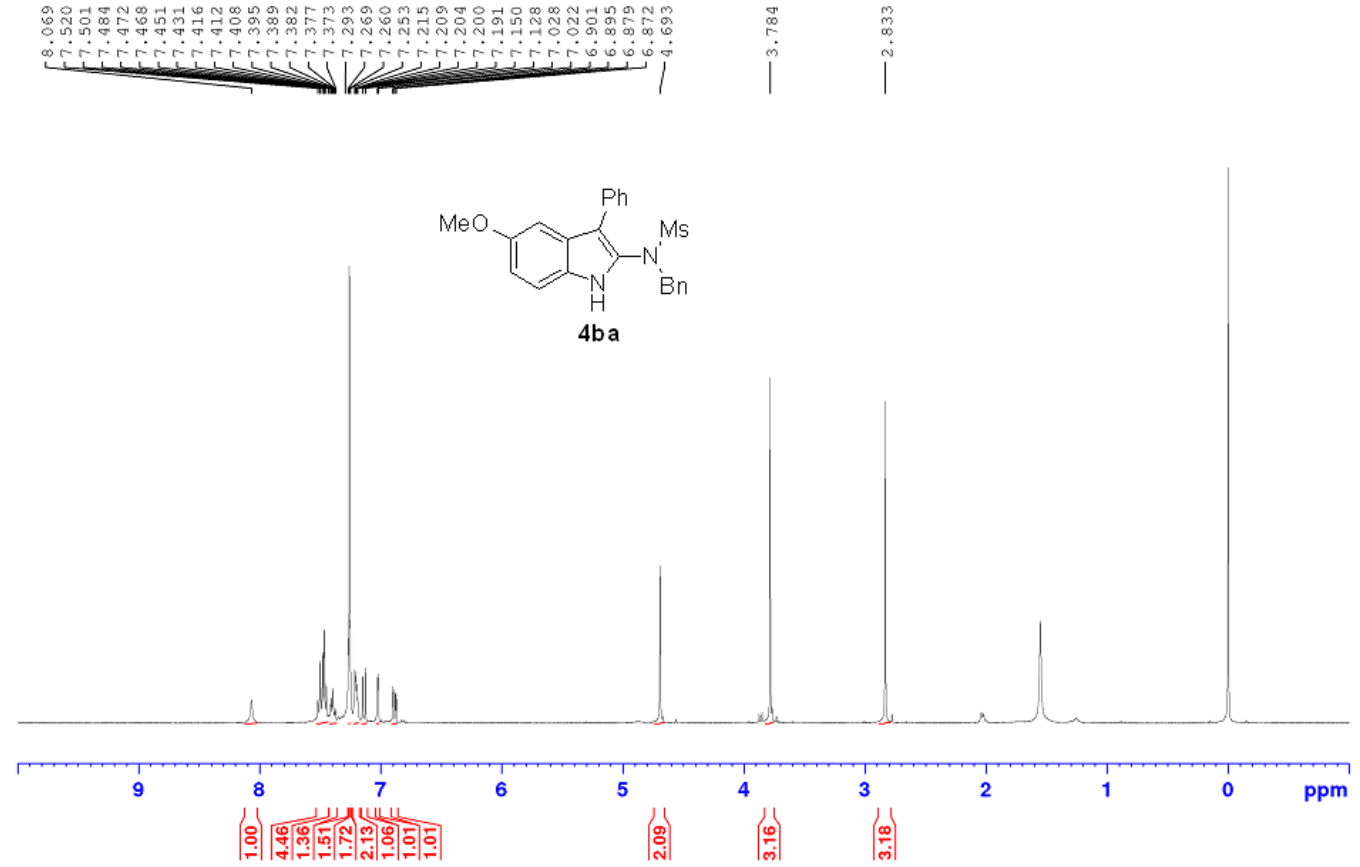


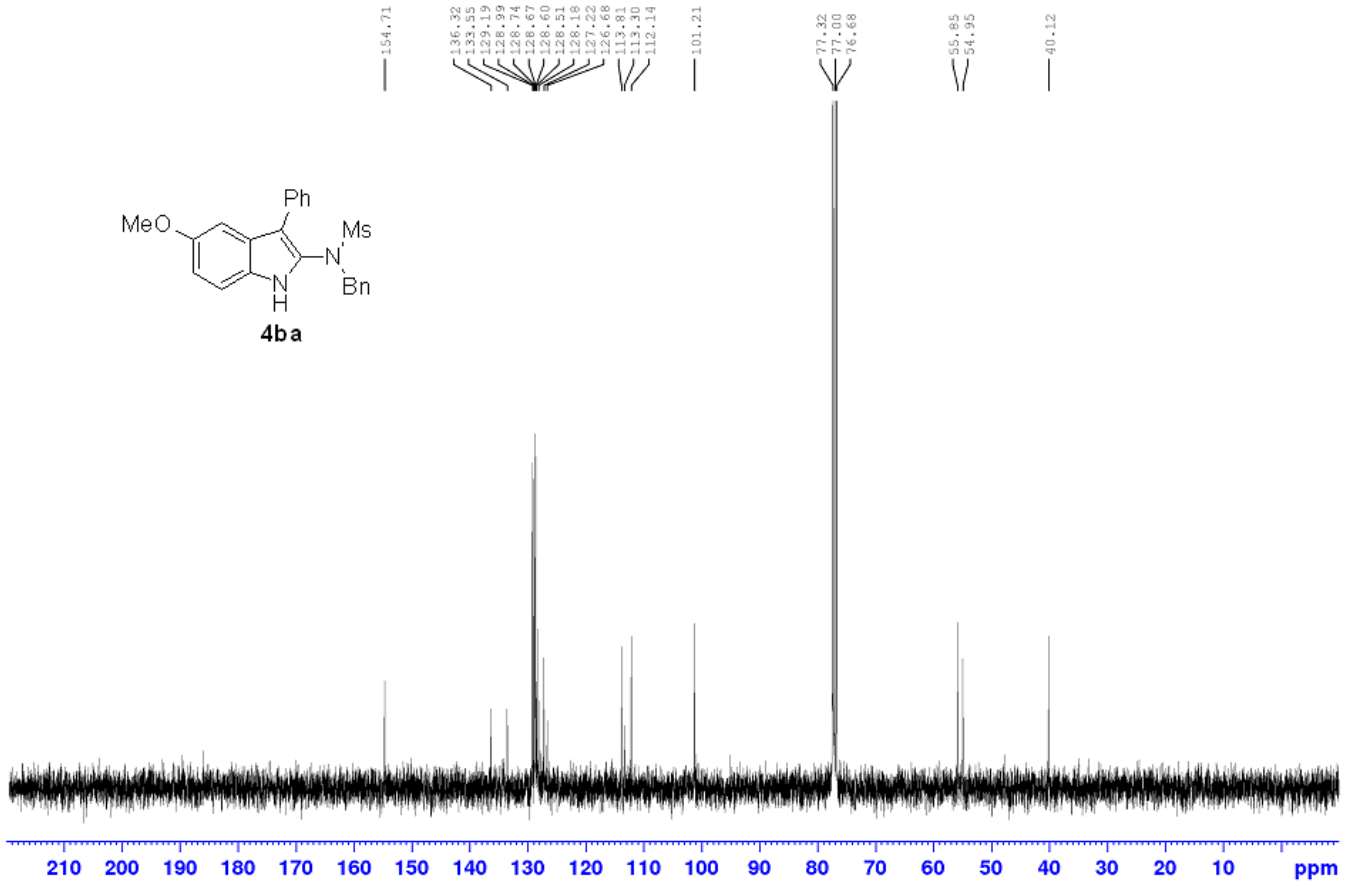
_N_-Benzyl-_N_-(3-phenyl-1_H_-indol-2-yl)methanesulfonamide (4aa)



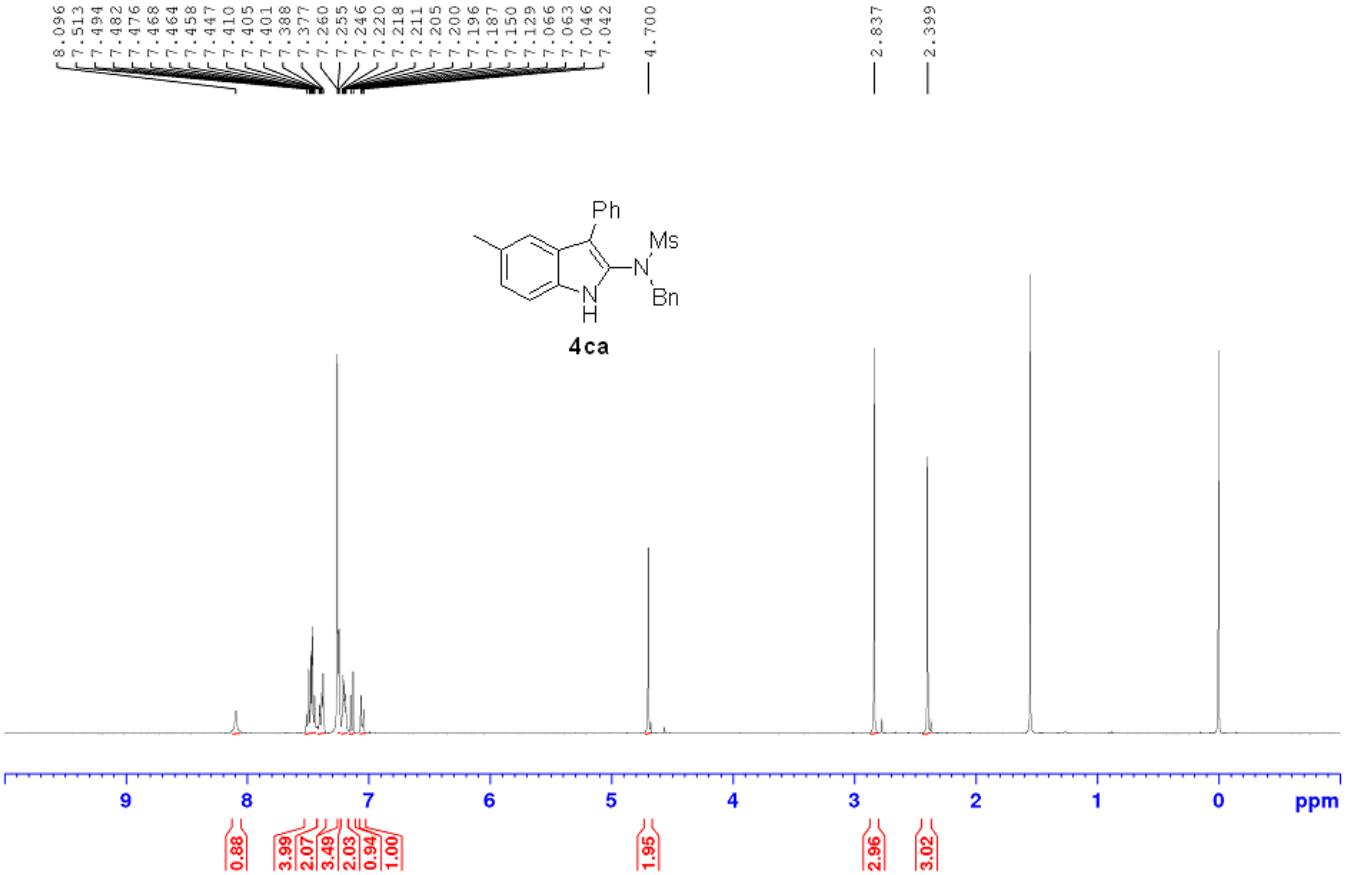


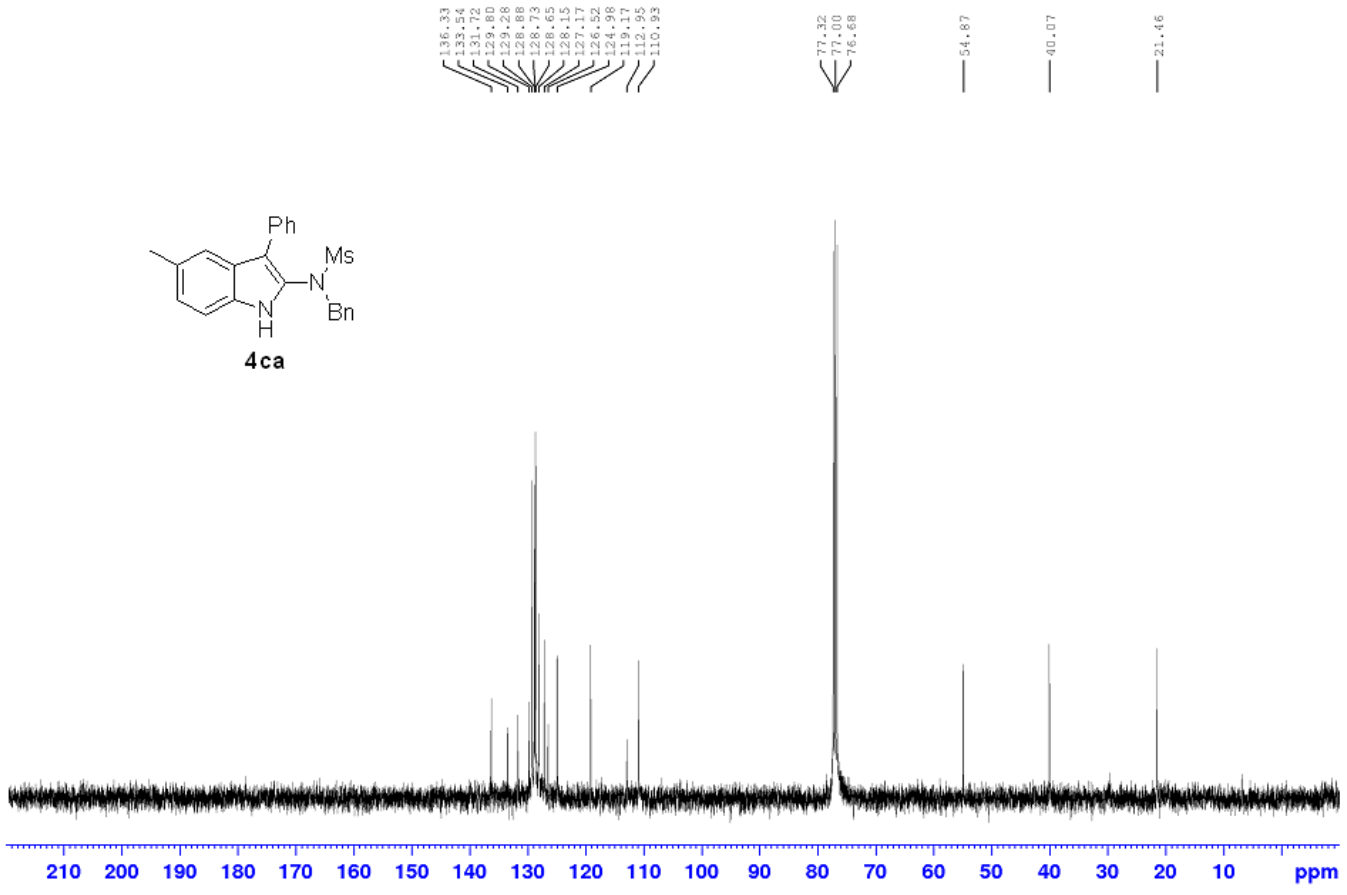
_N_-Benzyl-_N_-(5-methoxy-3-phenyl-1_H_-indol-2-yl)methanesulfonamide (4ba)



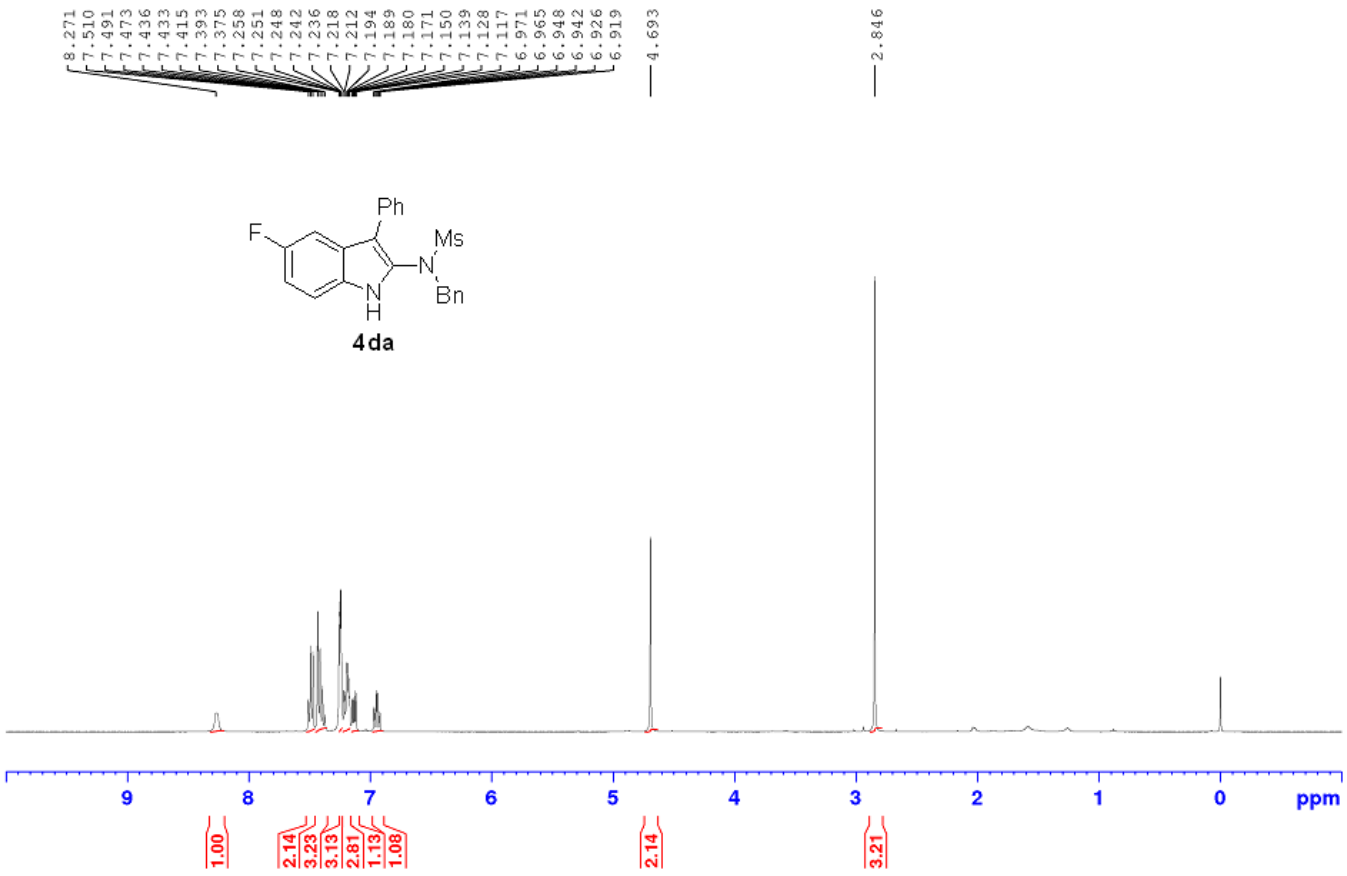


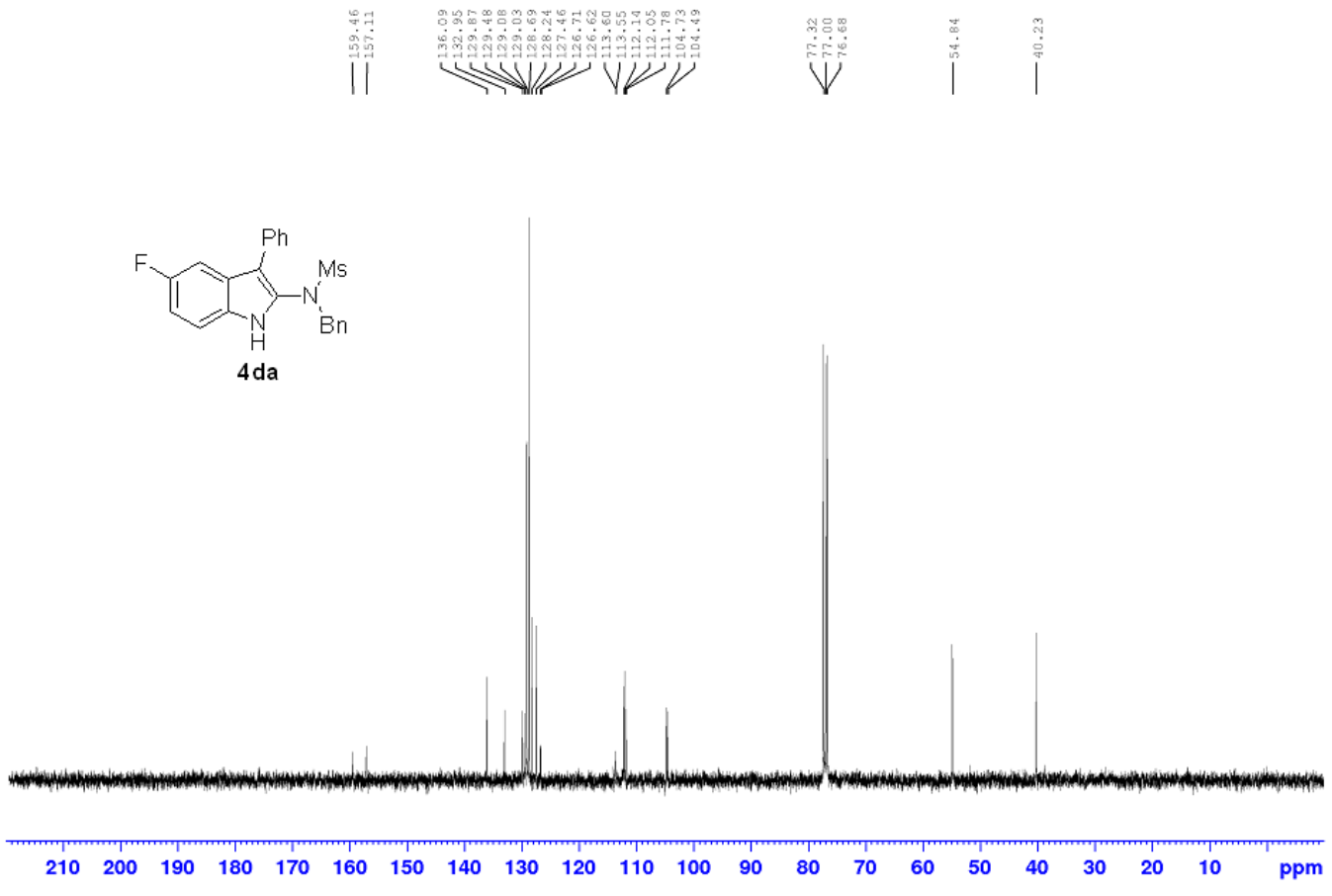
_N_-Benzyl-_N_-(5-methyl-3-phenyl-1_H_-indol-2-yl)methanesulfonamide (4ca)



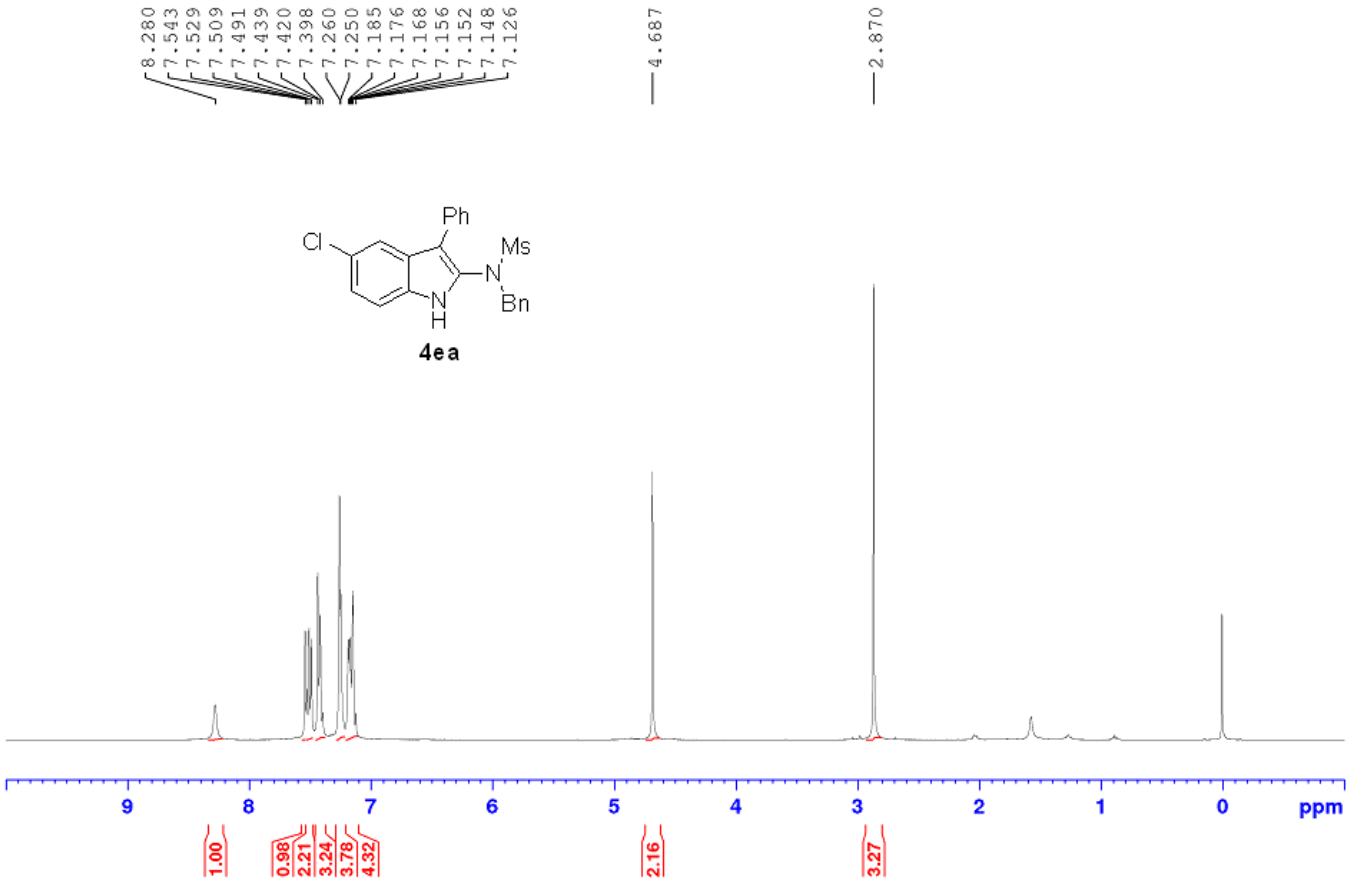


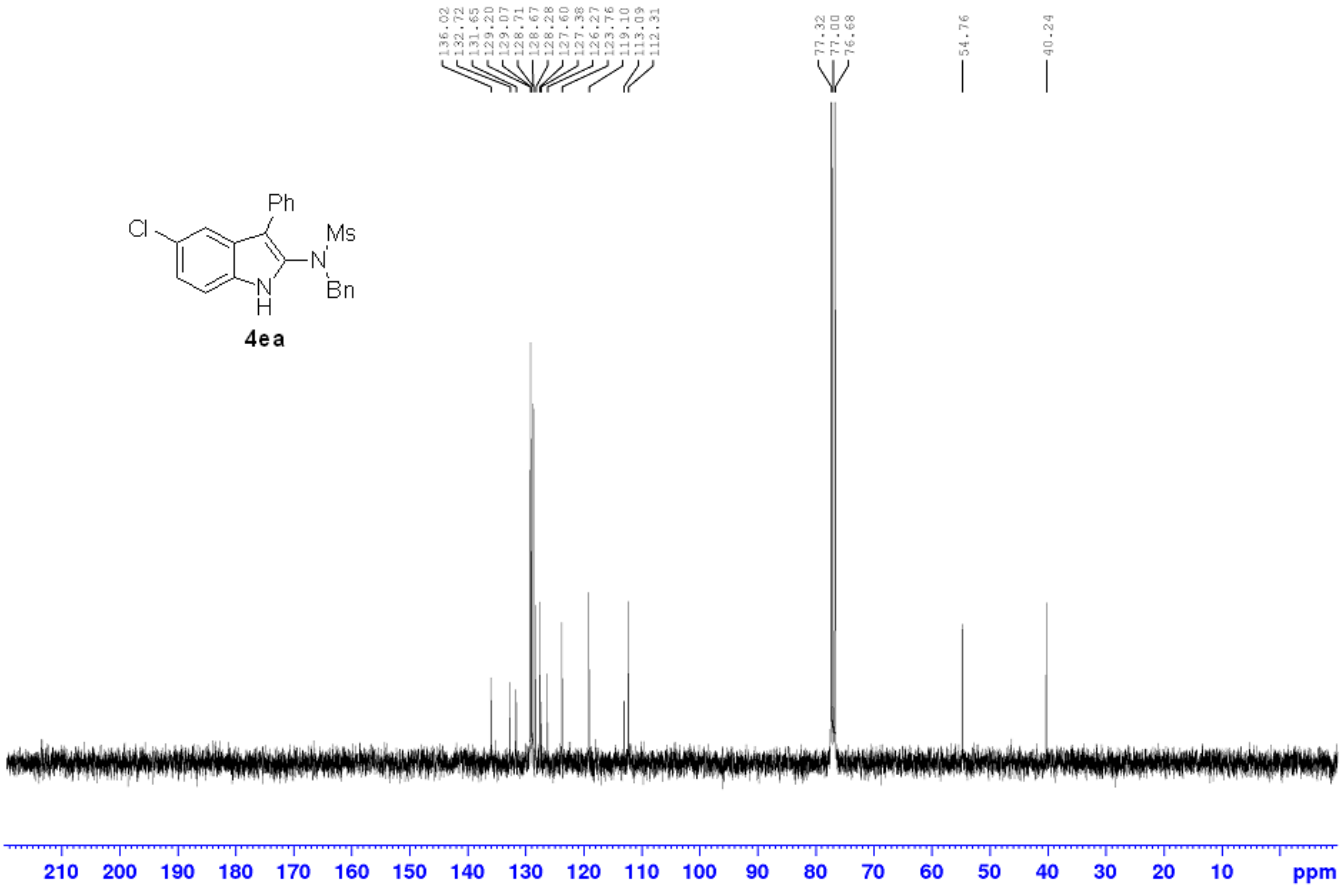
***N*-Benzyl-*N*-(5-fluoro-3-phenyl-1*H*-indol-2-yl)methanesulfonamide (4da)**



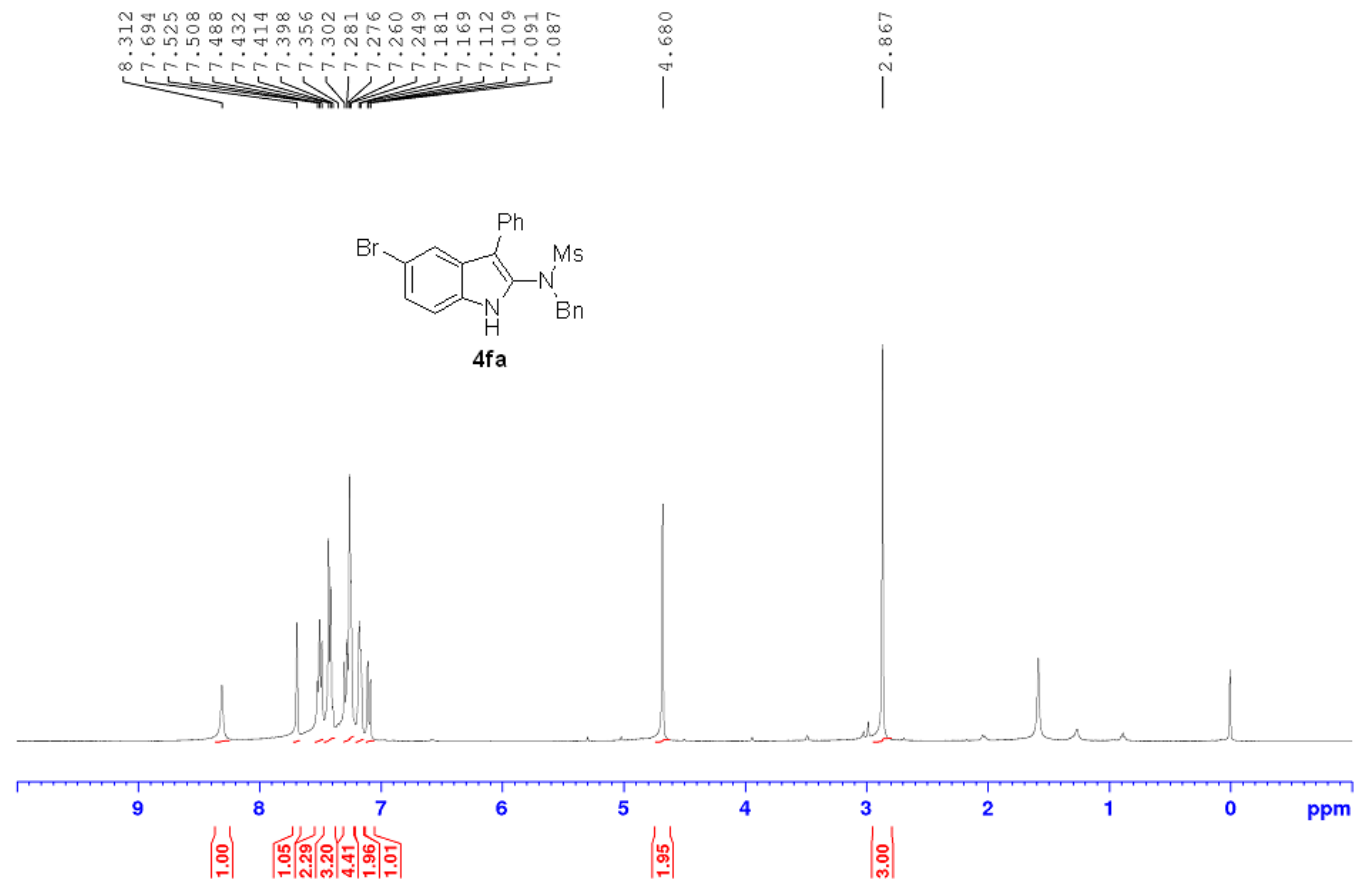


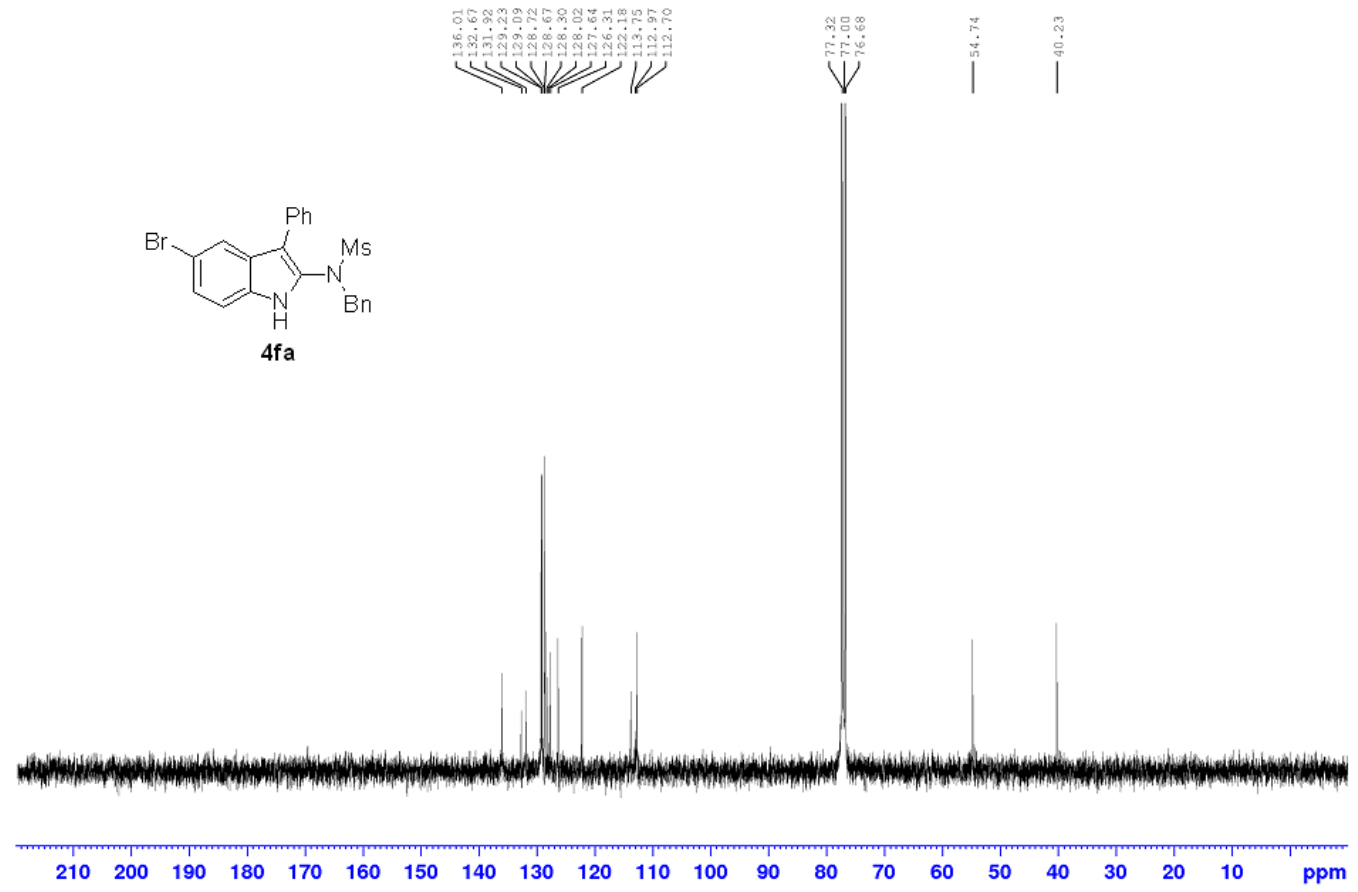
_N_-Benzyl-_N_-(5-chloro-3-phenyl-1_H_-indol-2-yl)methanesulfonamide (4ea)



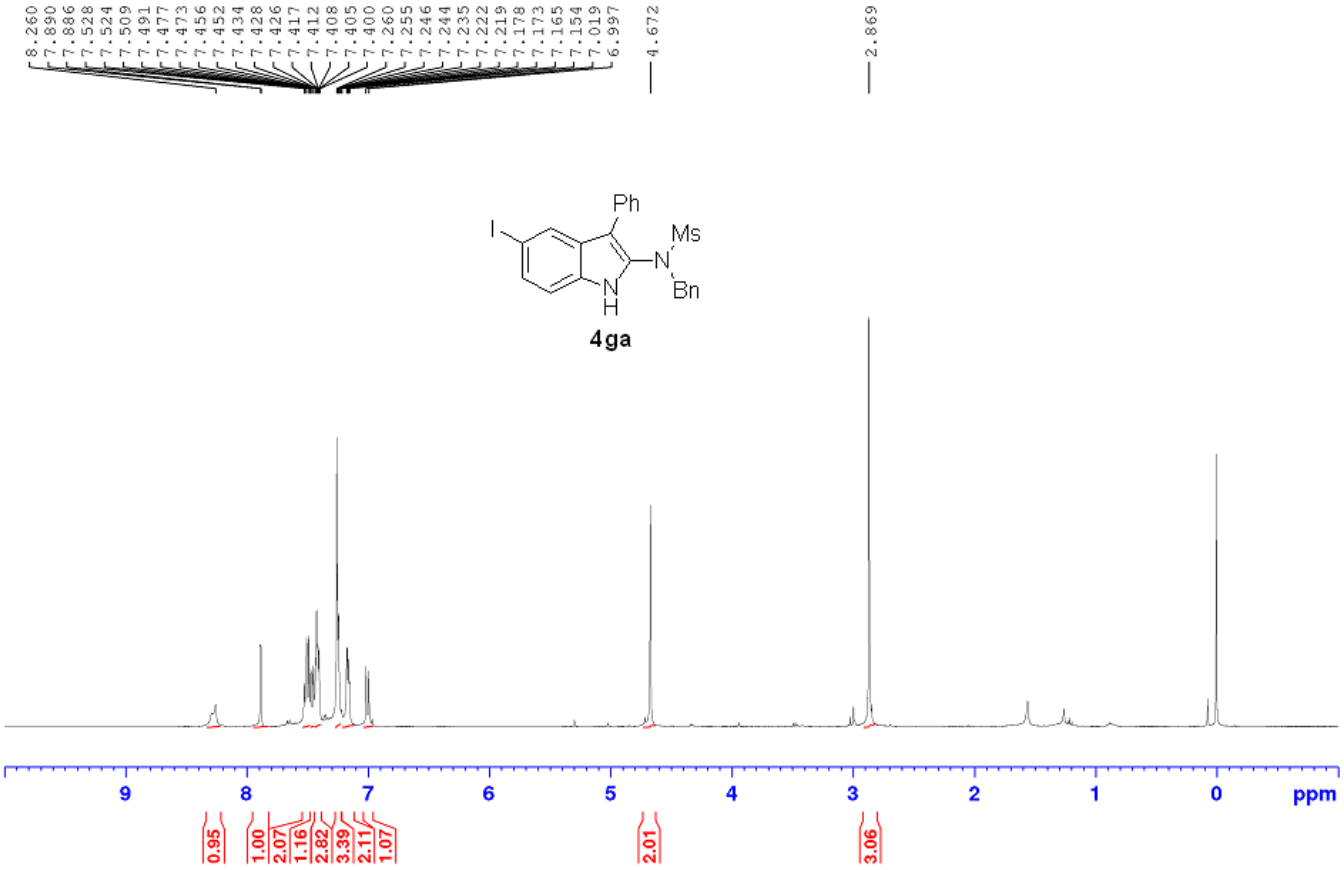


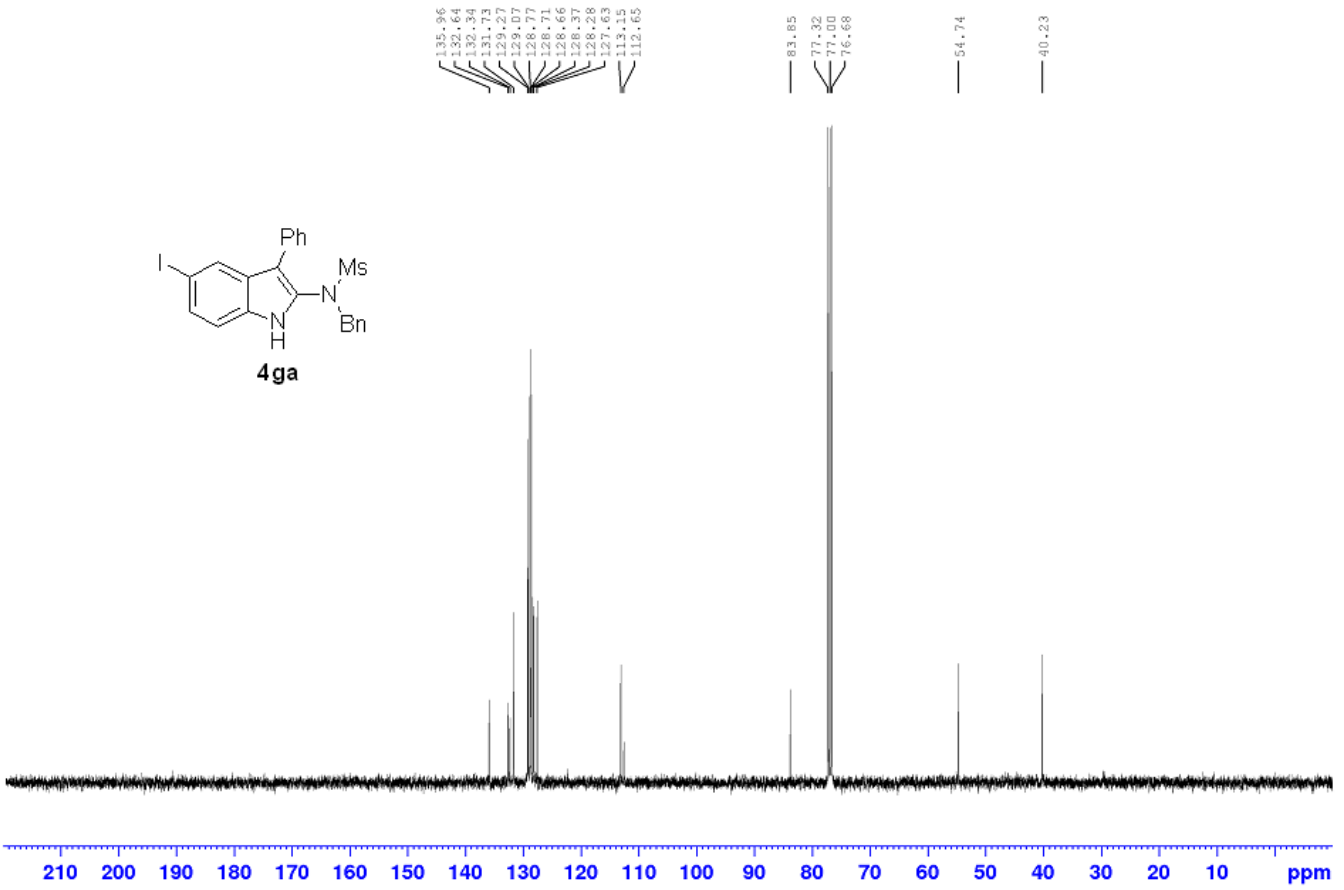
_N_-Benzyl-_N_-(5-bromo-3-phenyl-1_H_-indol-2-yl)methanesulfonamide (4fa)



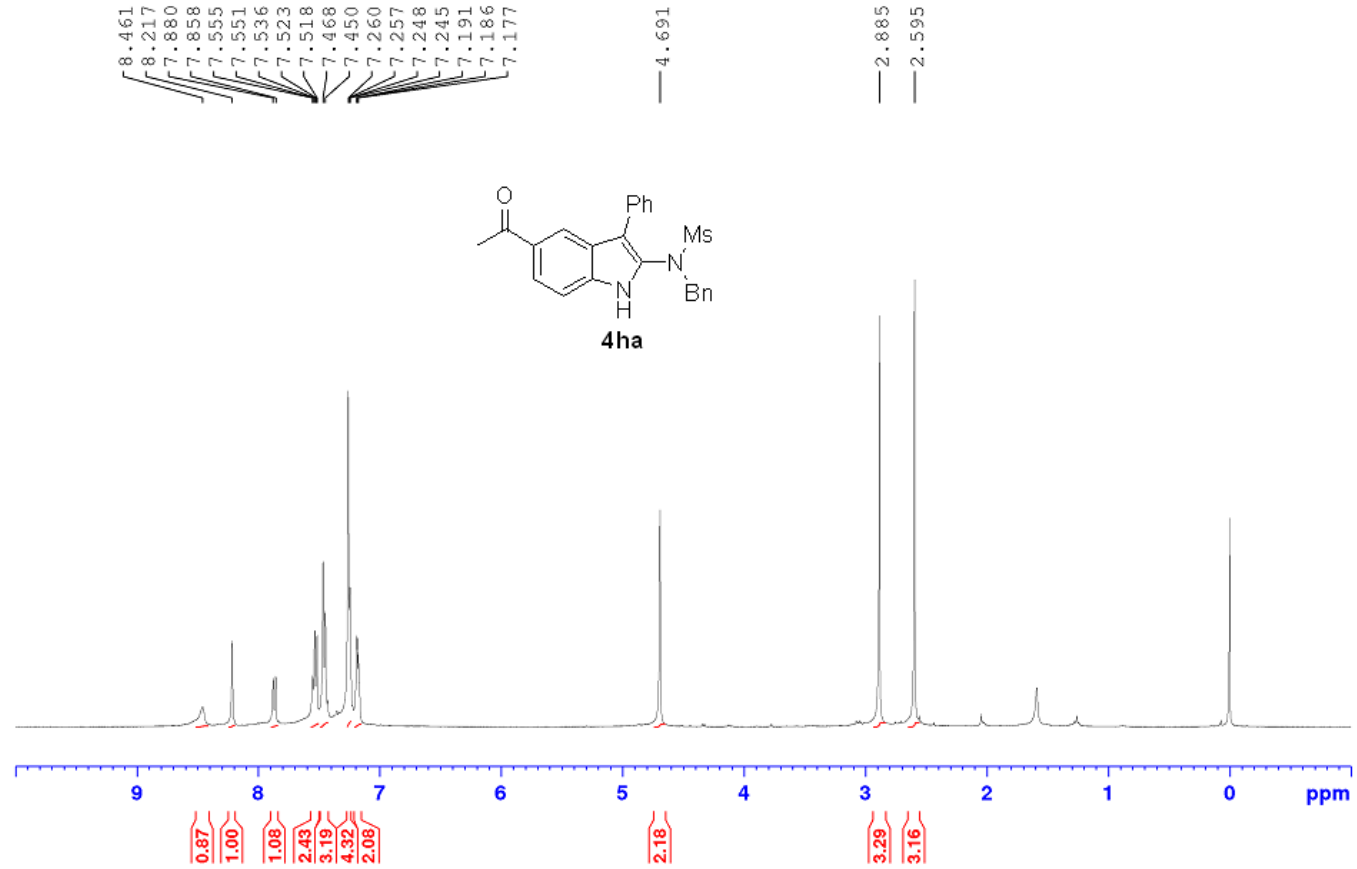


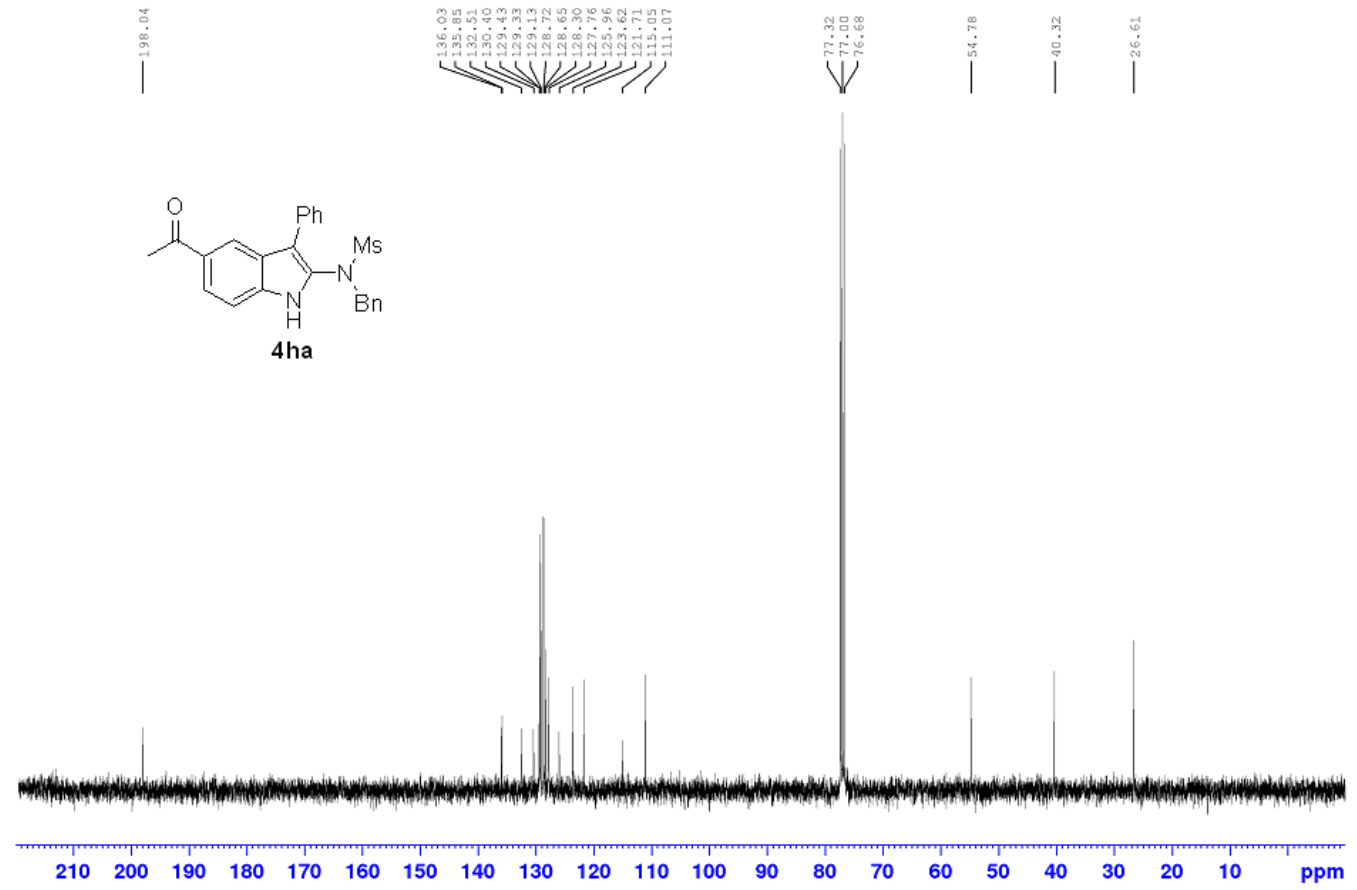
_N_-Benzyl-_N_-(5-iodo-3-phenyl-1_H_-indol-2-yl)methanesulfonamide (4ga)



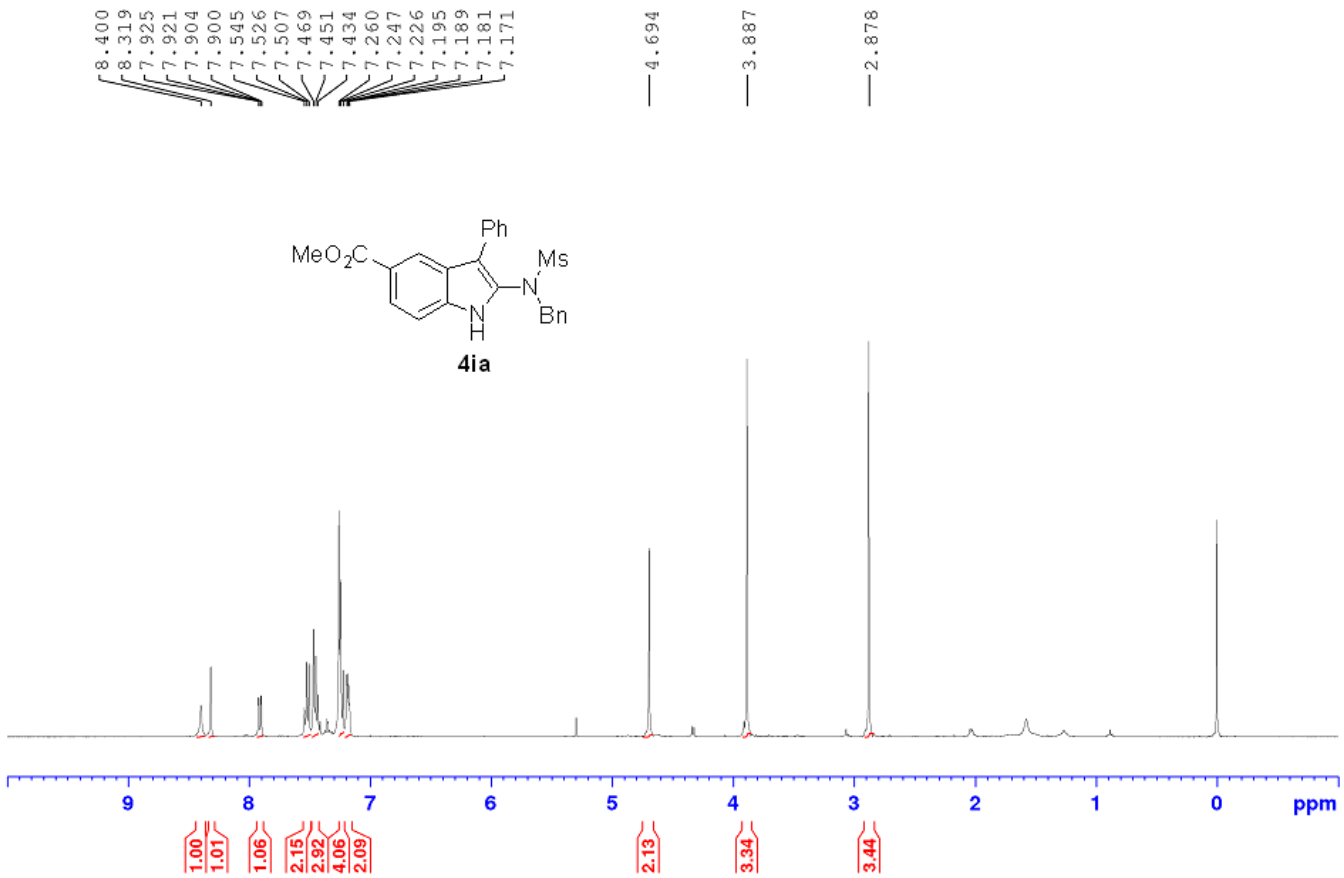


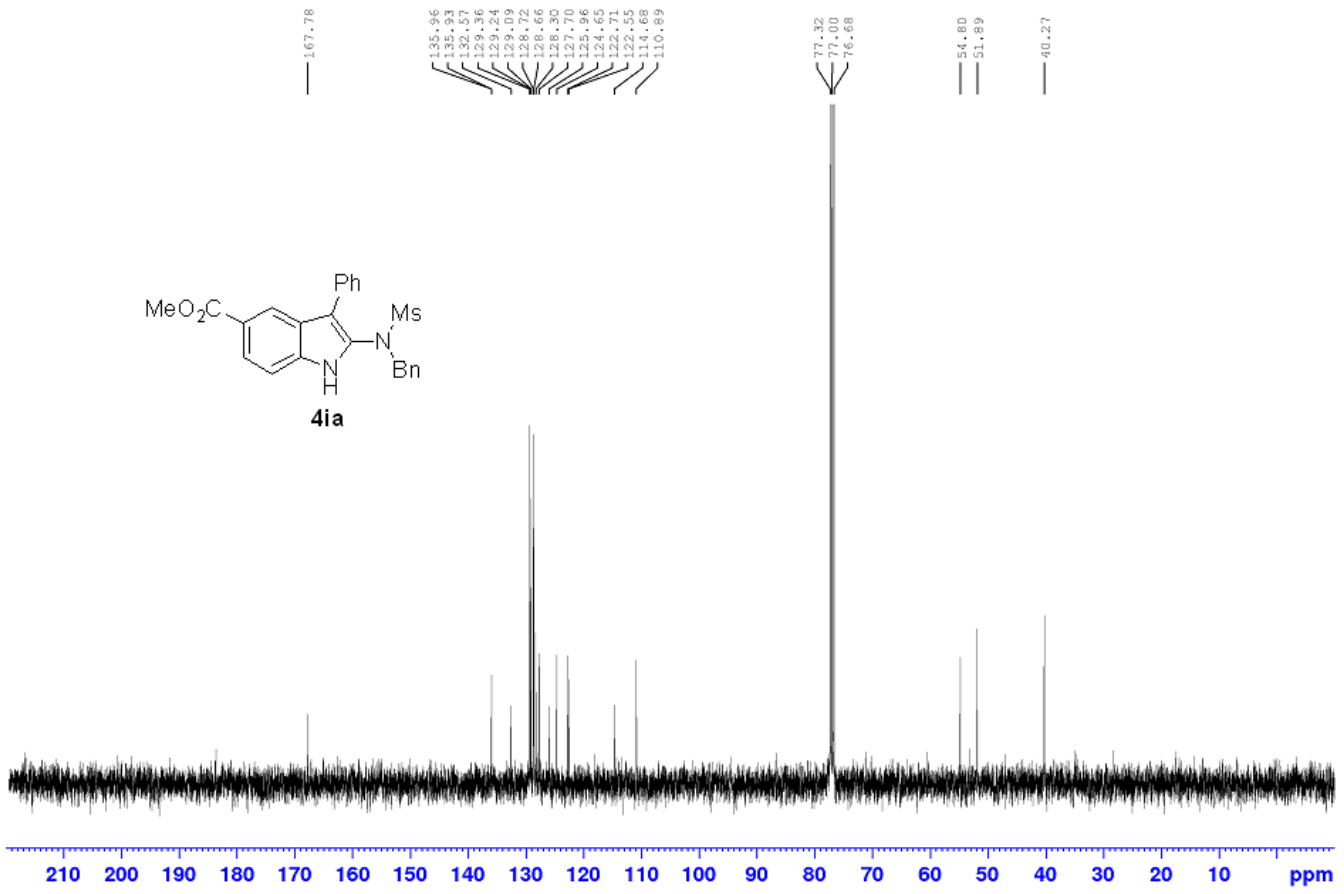
***N*-(5-Acetyl-3-phenyl-1*H*-indol-2-yl)-*N*-benzylmethanesulfonamide (4ha)**



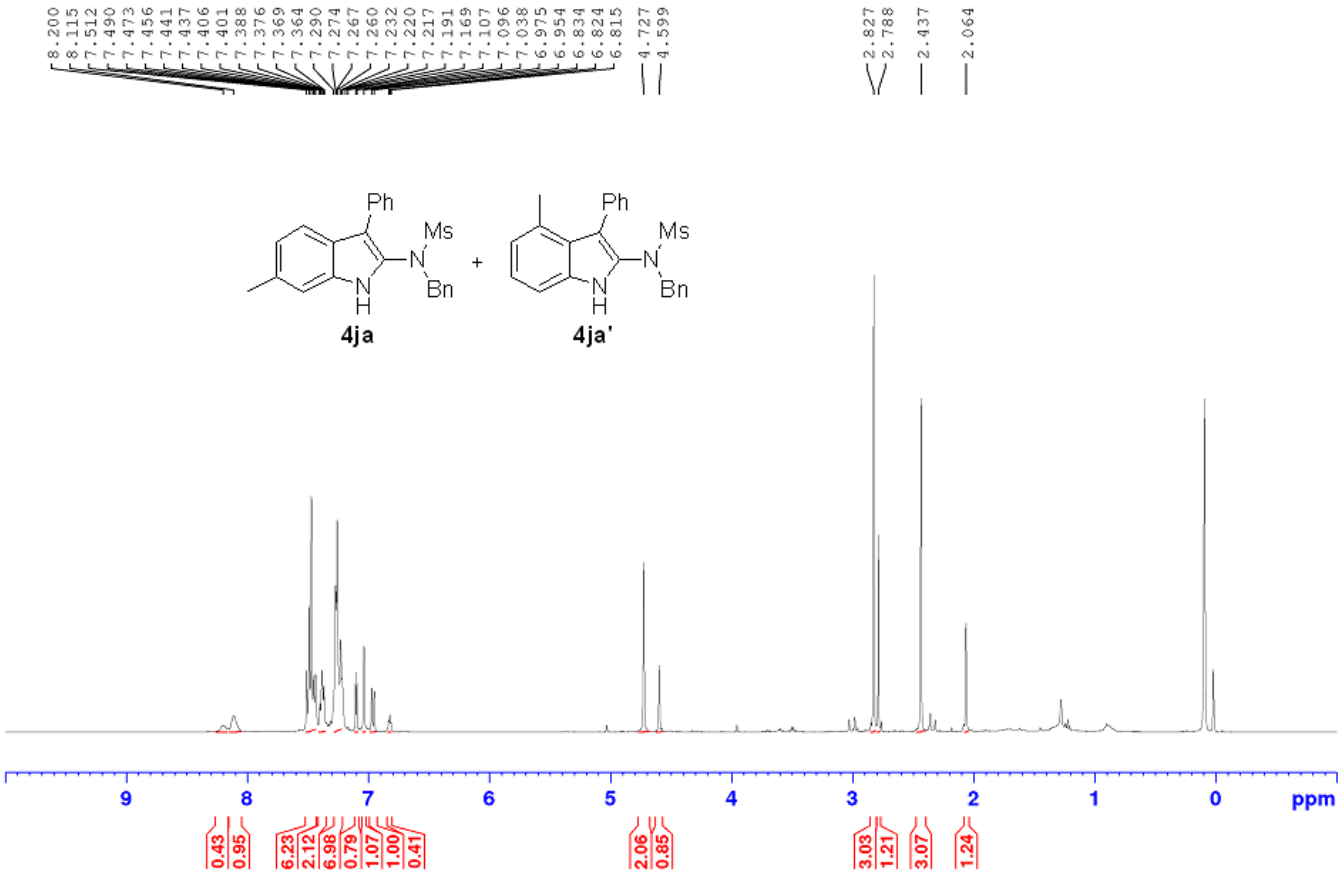


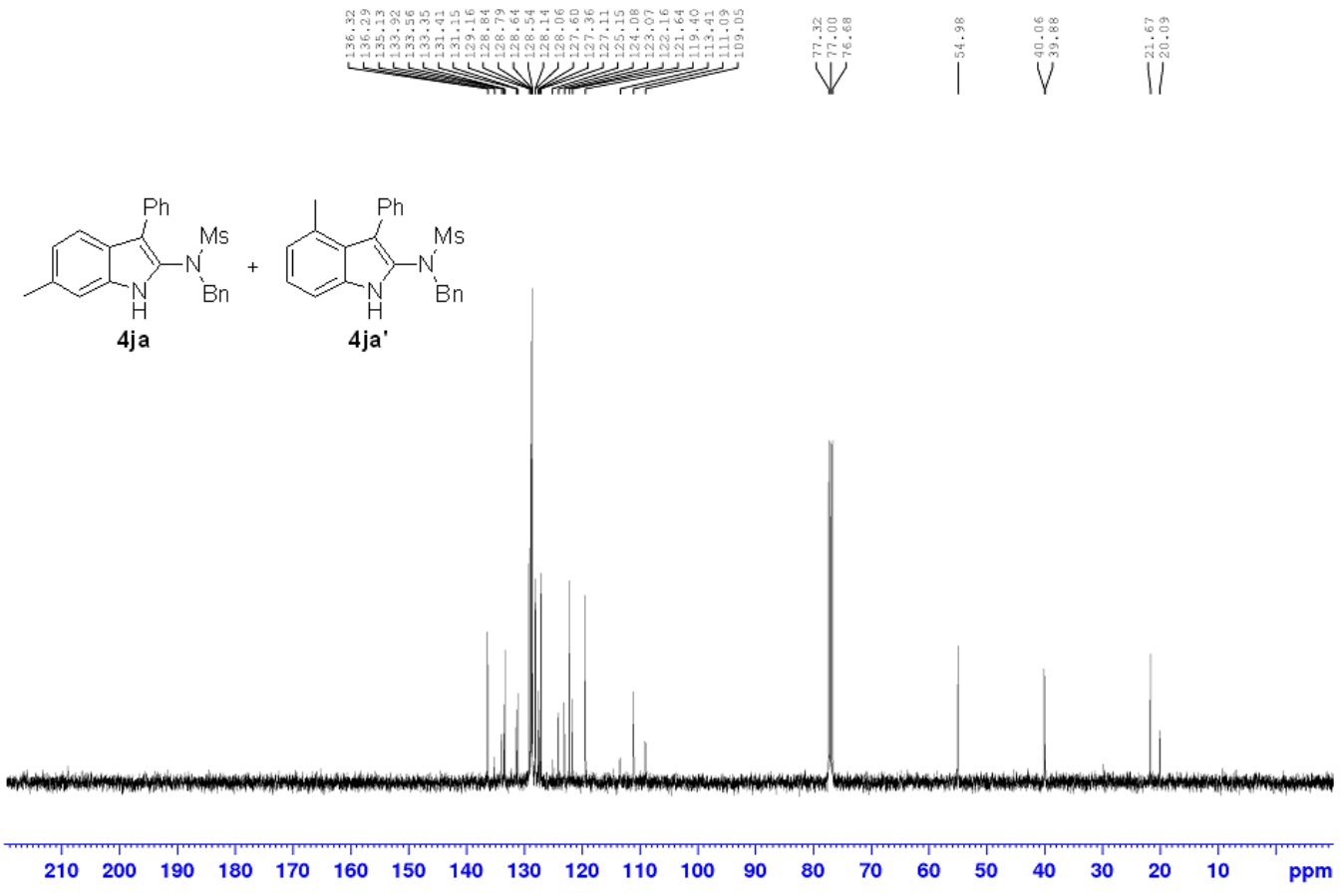
Methyl 2-(*N*-Benzylmethylsulfonamido)-3-phenyl-1*H*-indole-5-carboxylate (4ia)



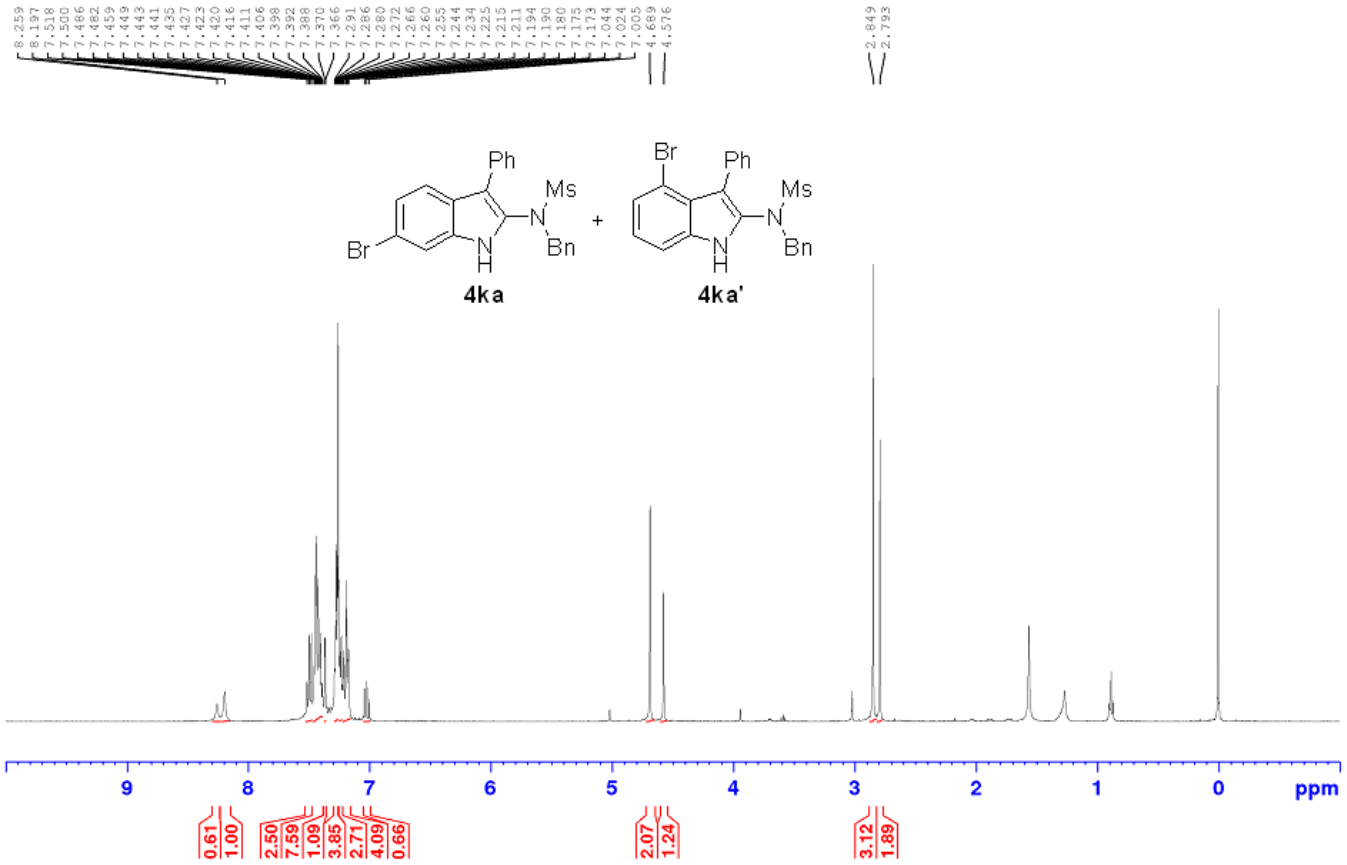


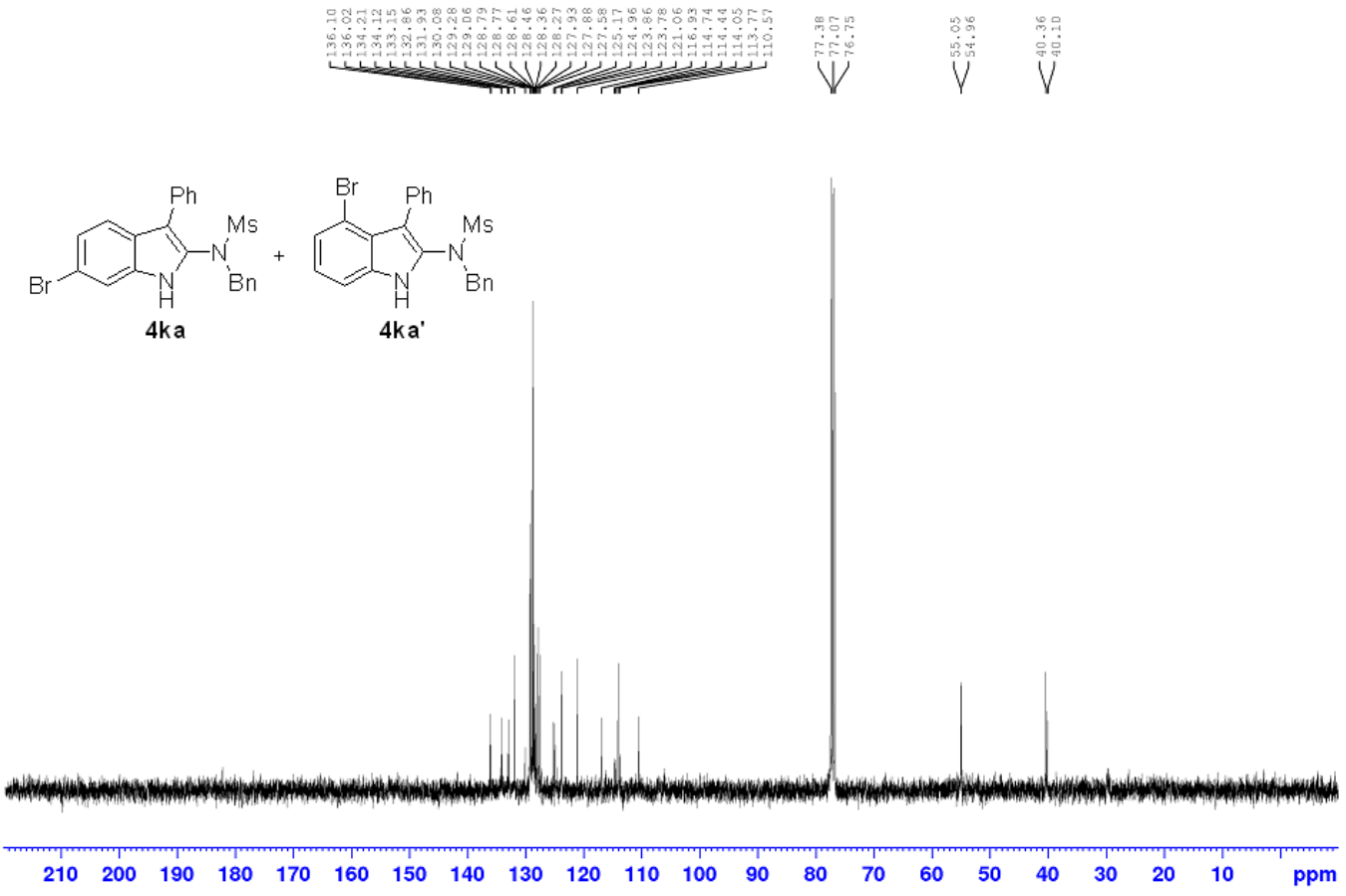
_N_-Benzyl-_N_-(6-methyl-3-phenyl-1_H_-indol-2-yl)methanesulfonamide (4ja) & _N_-Benzyl-_N_-(4-methyl-3-phenyl-1_H_-indol-2-yl)methanesulfonamide (4ja′)



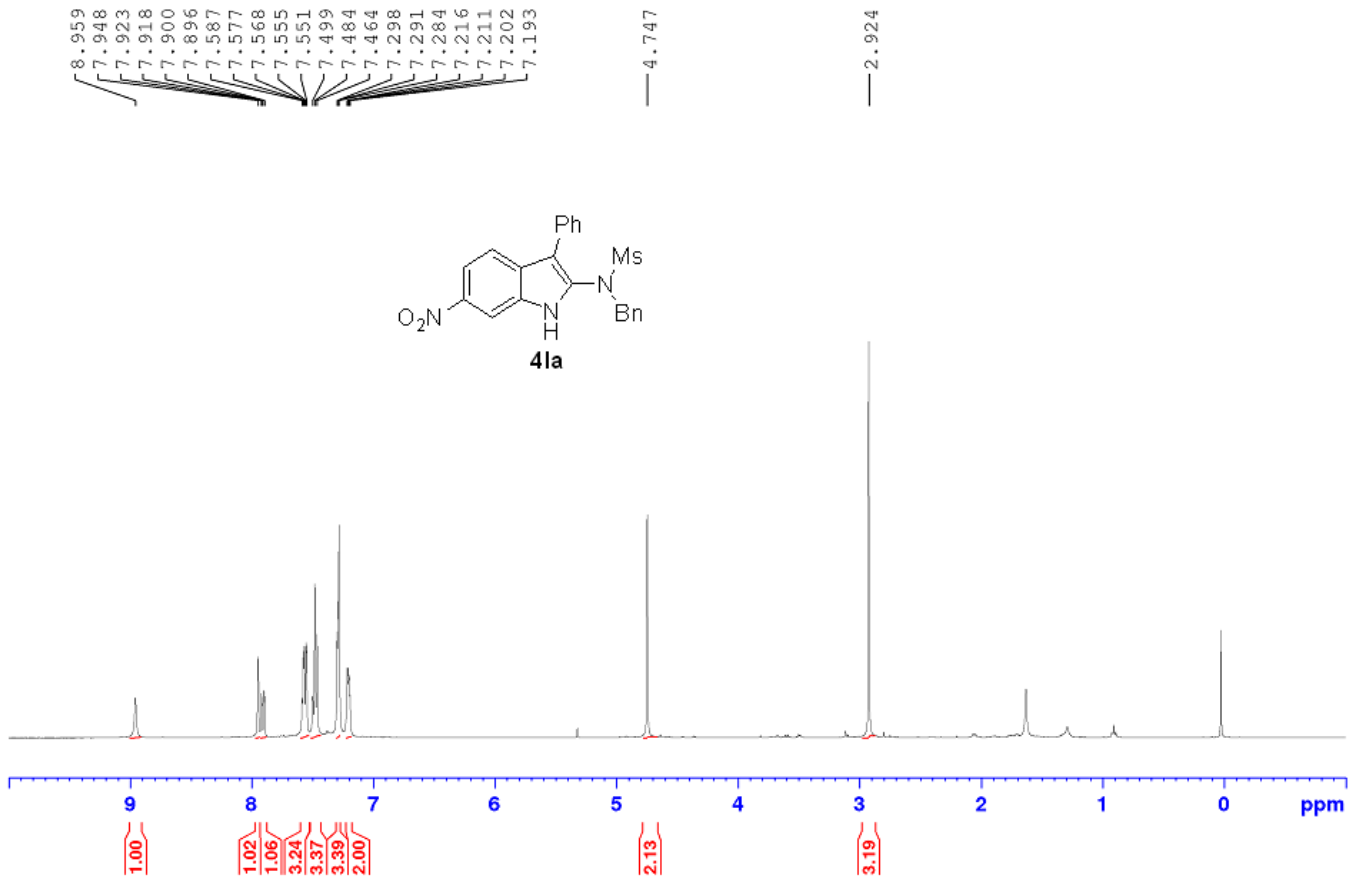


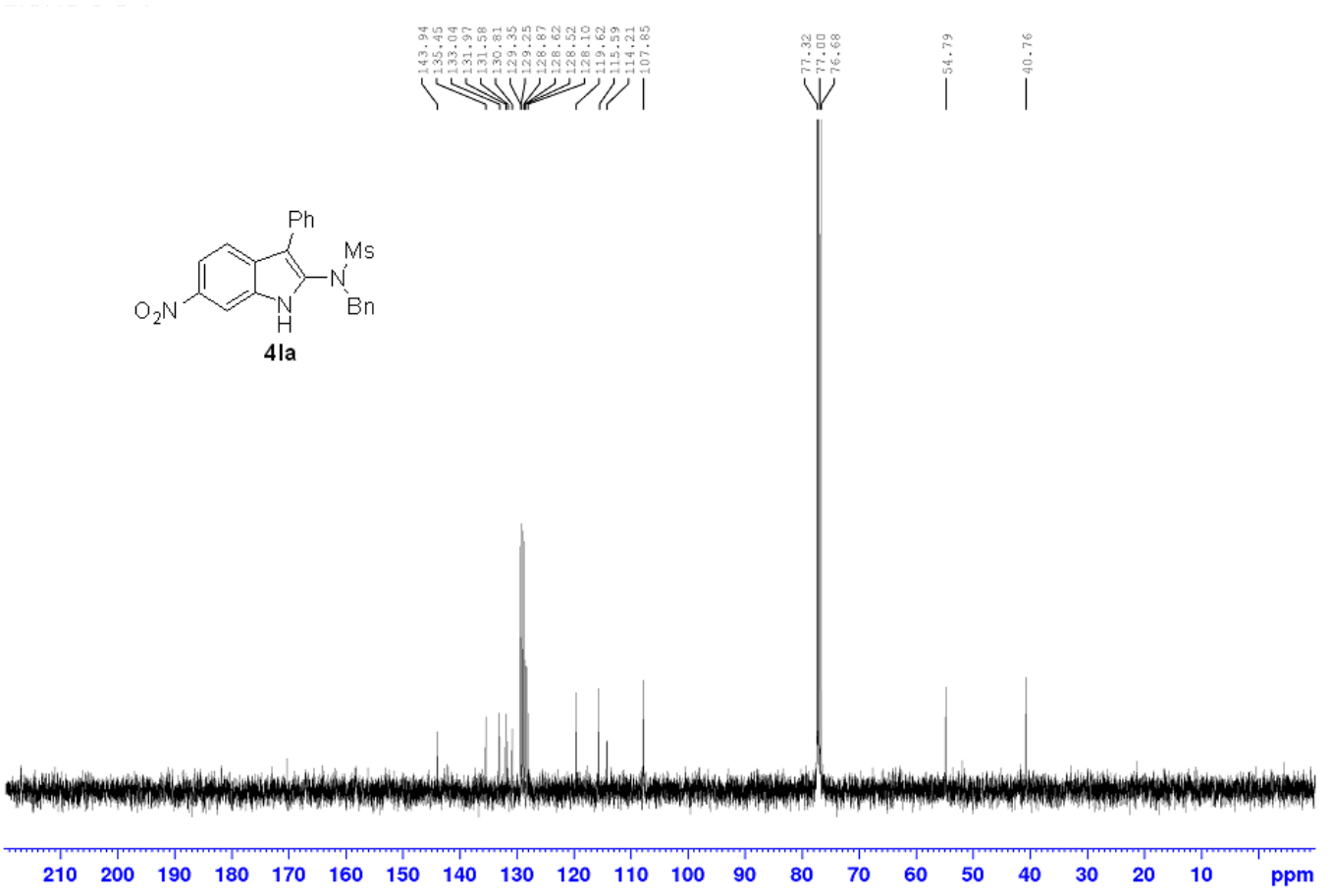
***N*-Benzyl-*N*-(6-bromo-3-phenyl-1*H*-indol-2-yl)methanesulfonamide (4ka) & *N*-Benzyl-*N*-(4-bromo-3-phenyl-1*H*-indol-2-yl)methanesulfonamide (4ka′)**



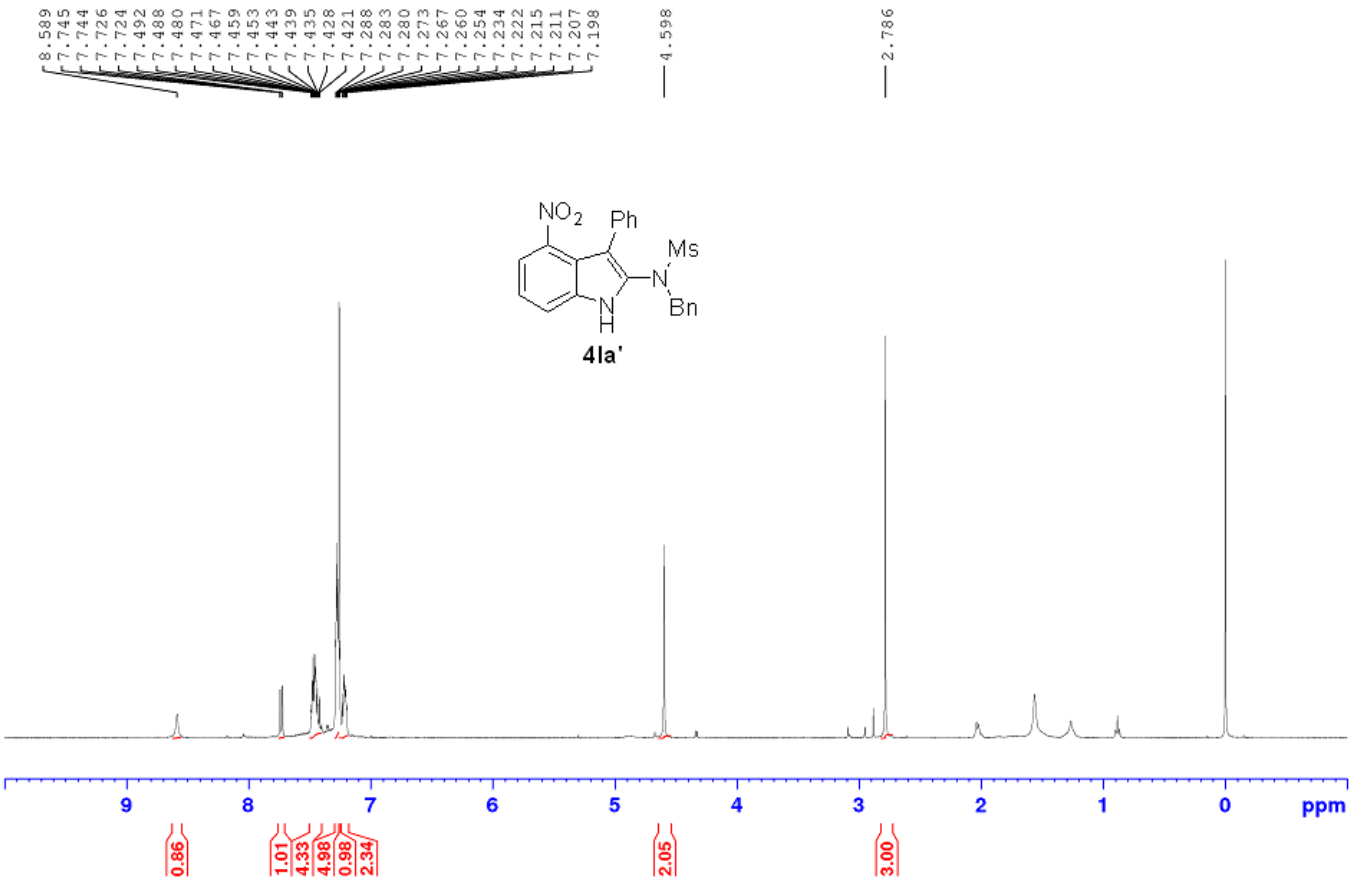


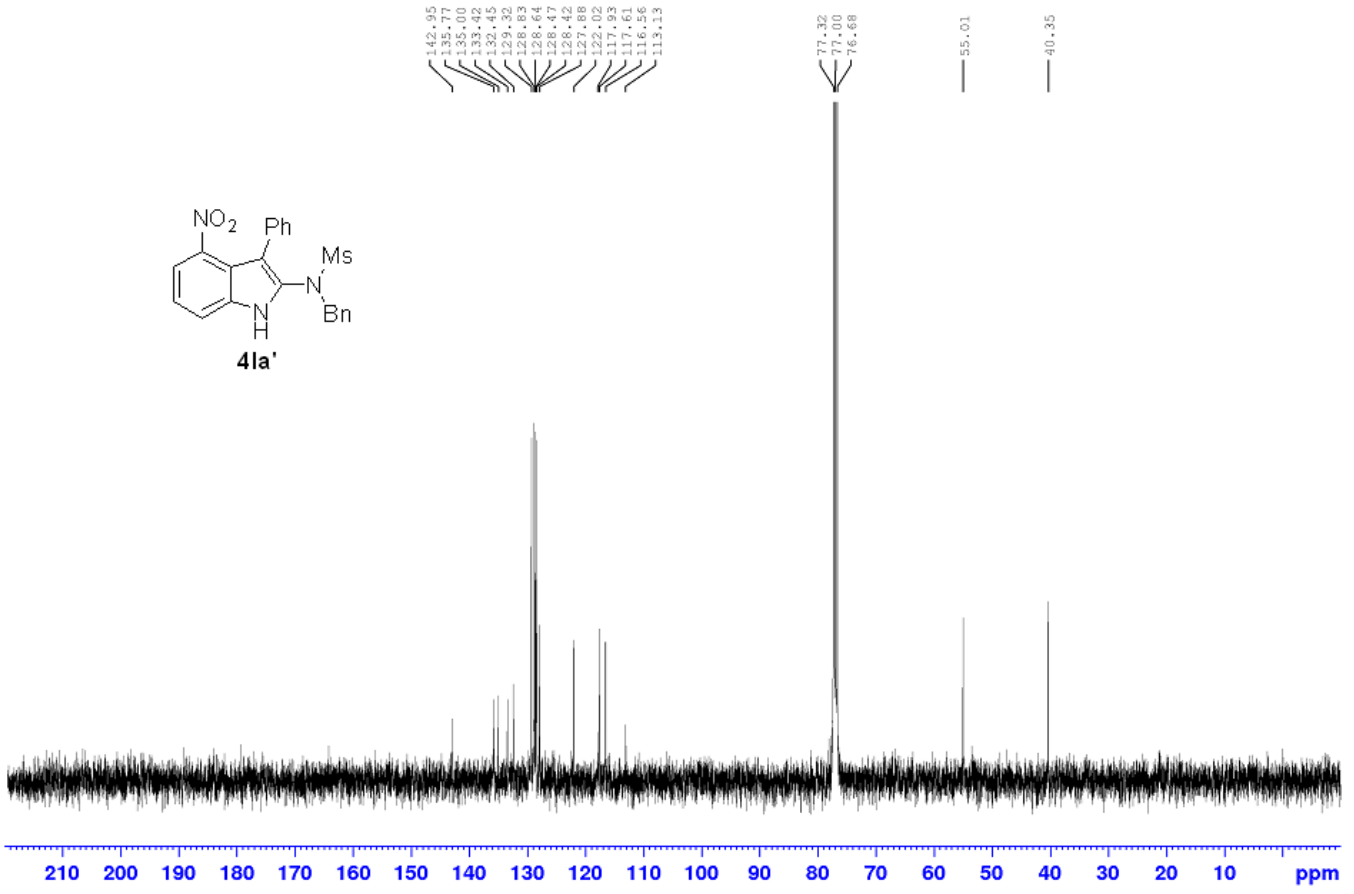
_N_-Benzyl-_N_-(6-nitro-3-phenyl-1_H_-indol-2-yl)methanesulfonamide (4la)



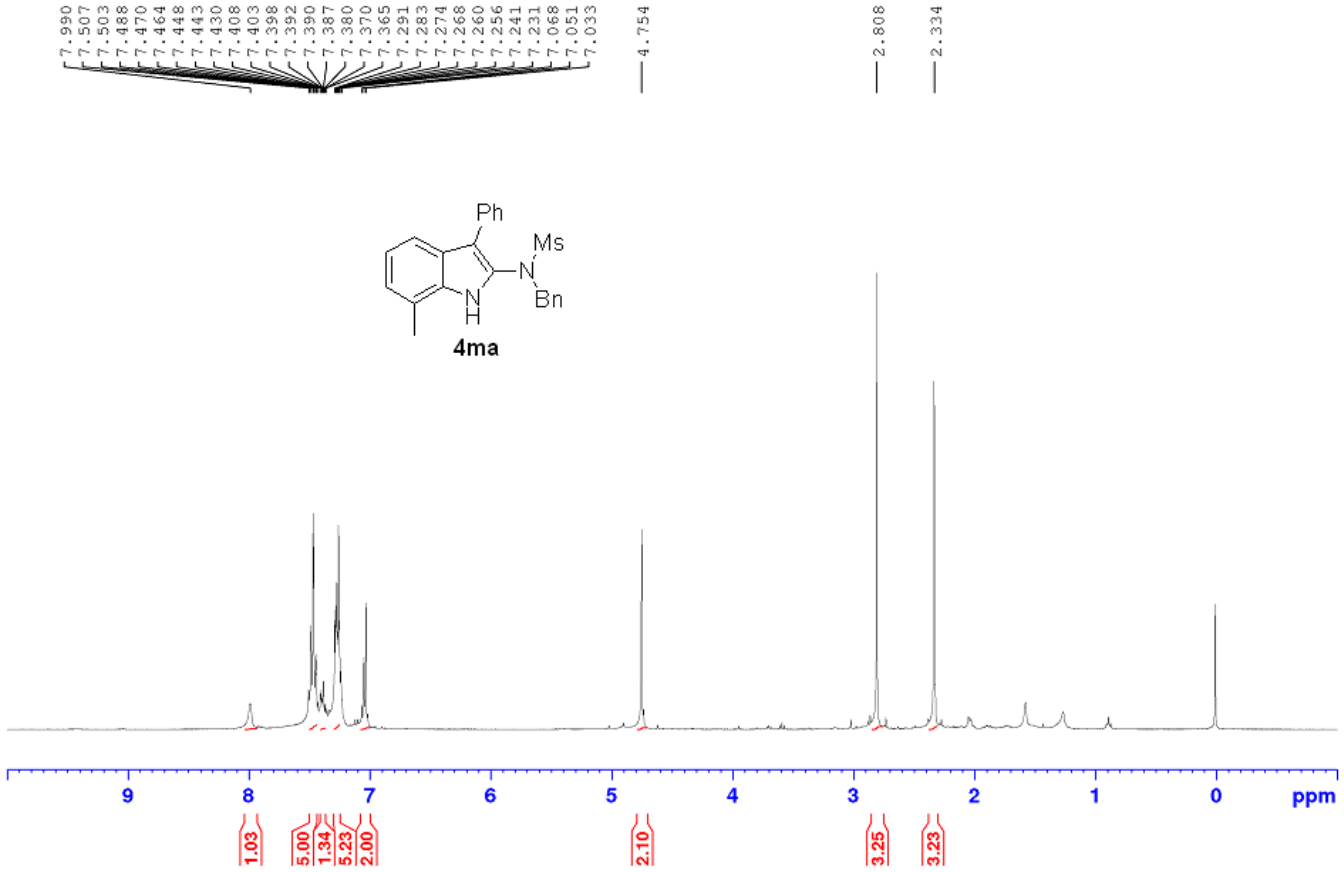


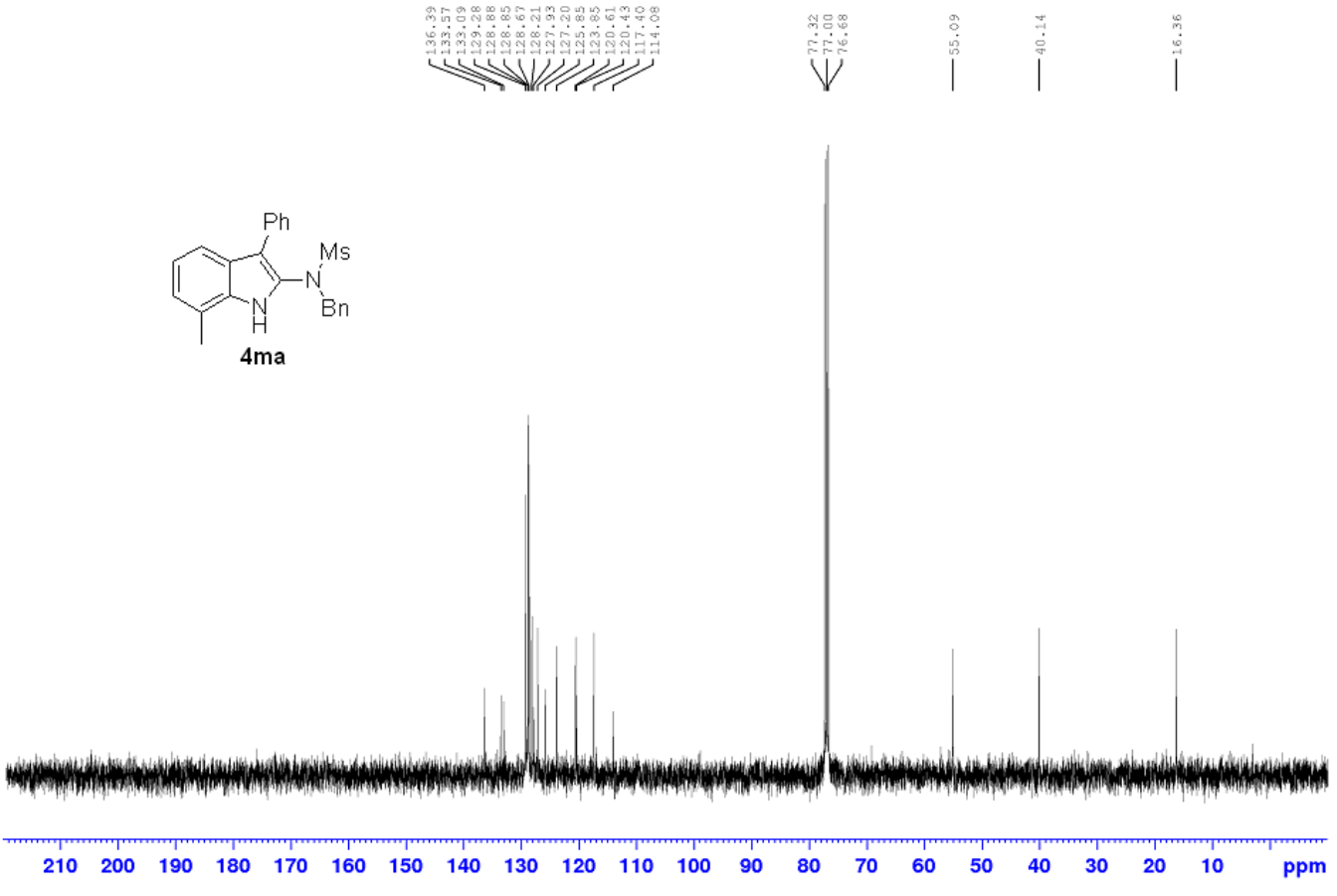
_N_-Benzyl-_N_-(4-nitro-3-phenyl-1_H_-indol-2-yl)methanesulfonamide (4la′)



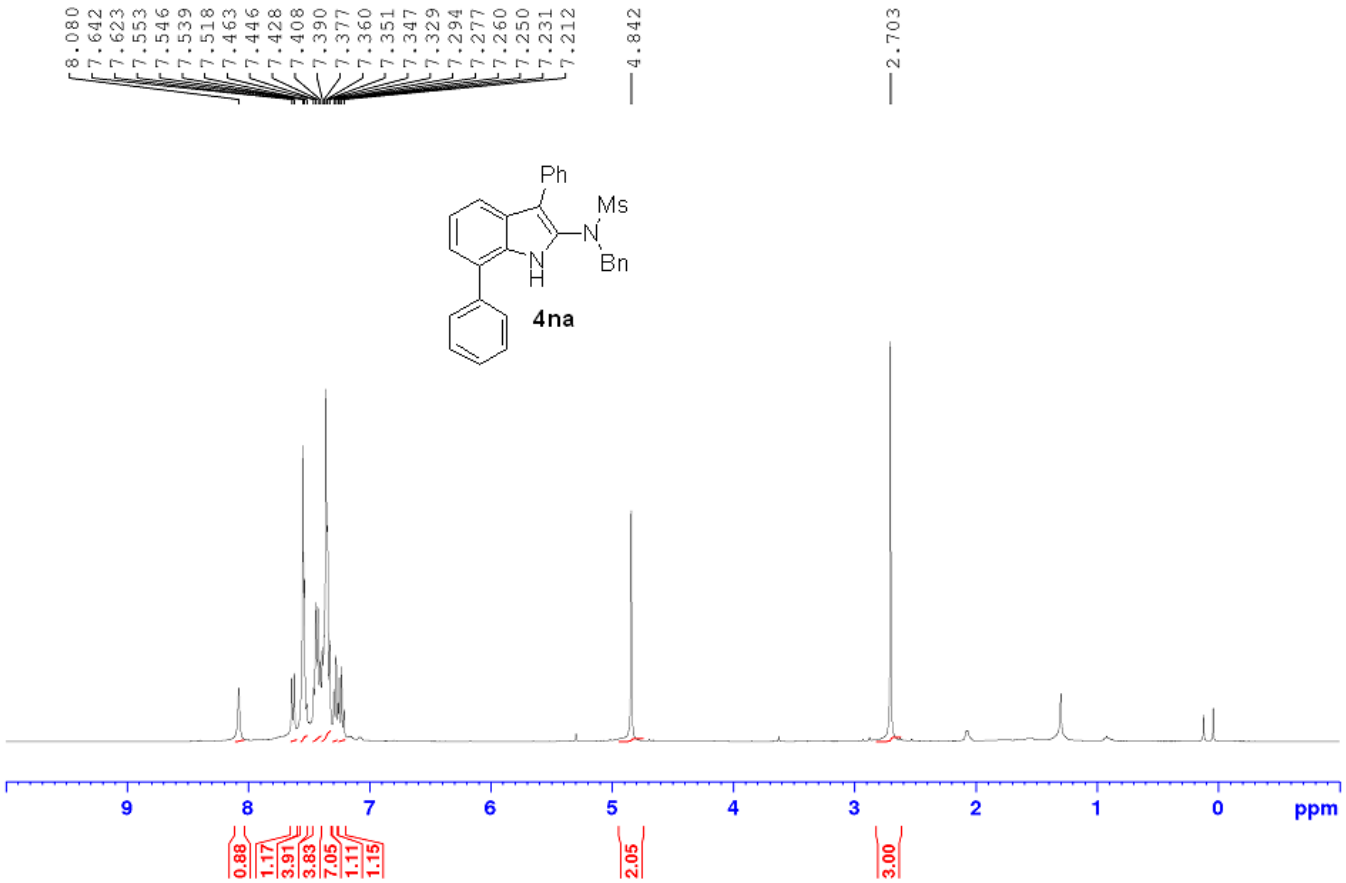


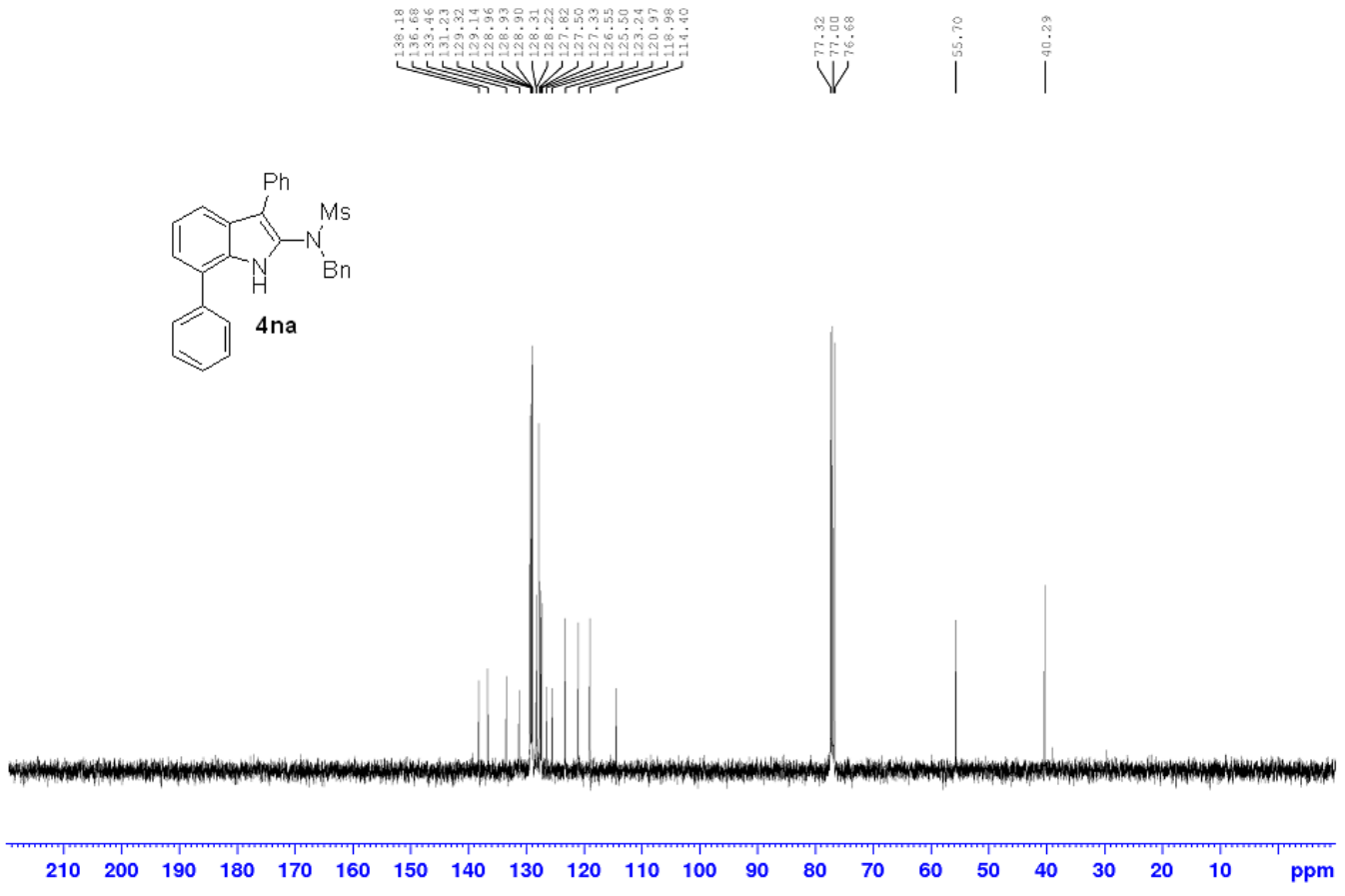
_N_-Benzyl-_N_-(7-methyl-3-phenyl-1_H_-indol-2-yl)methanesulfonamide (4ma)



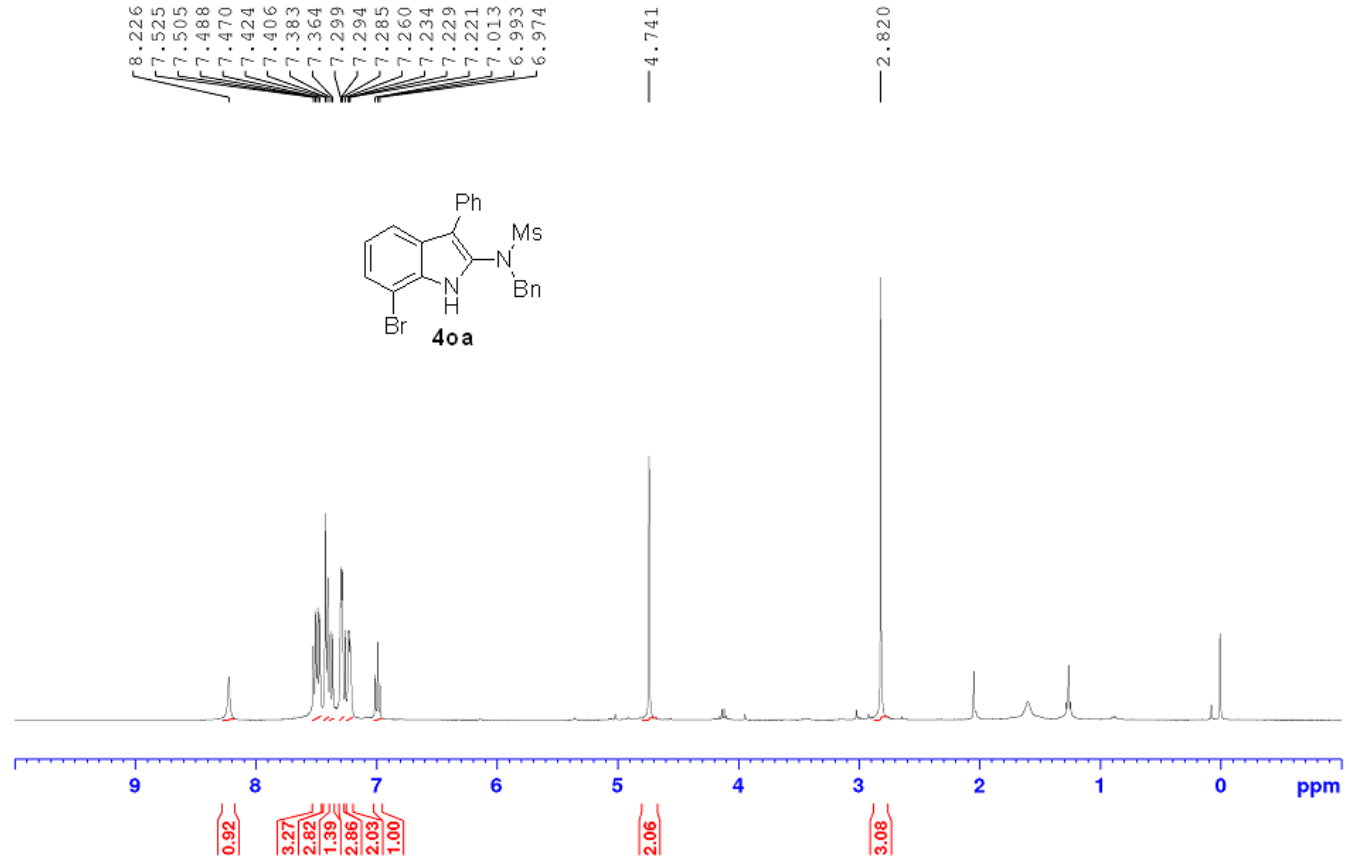


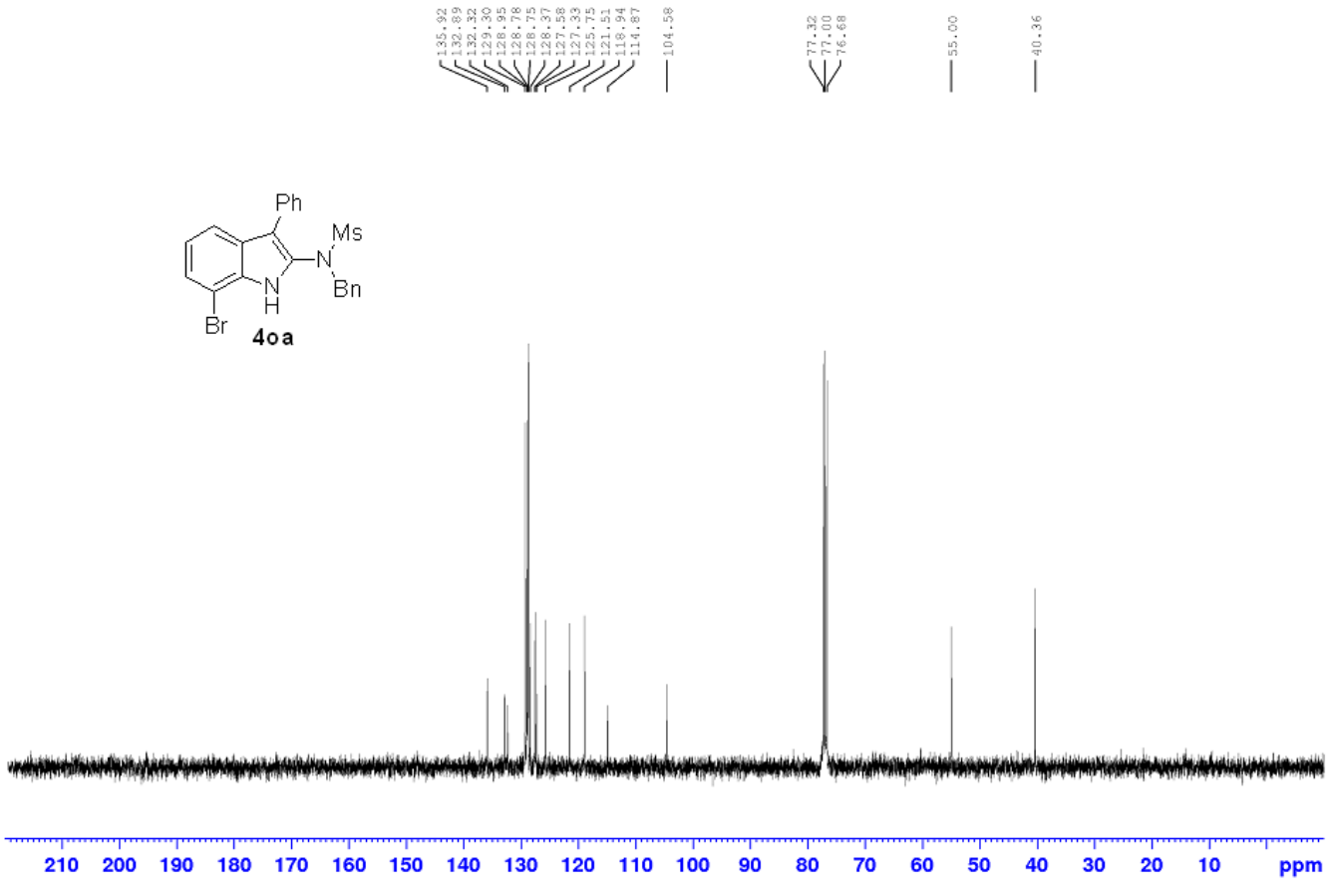
_N_-Benzyl-_N_-(3,7-diphenyl-1_H_-indol-2-yl)methanesulfonamide (4na)



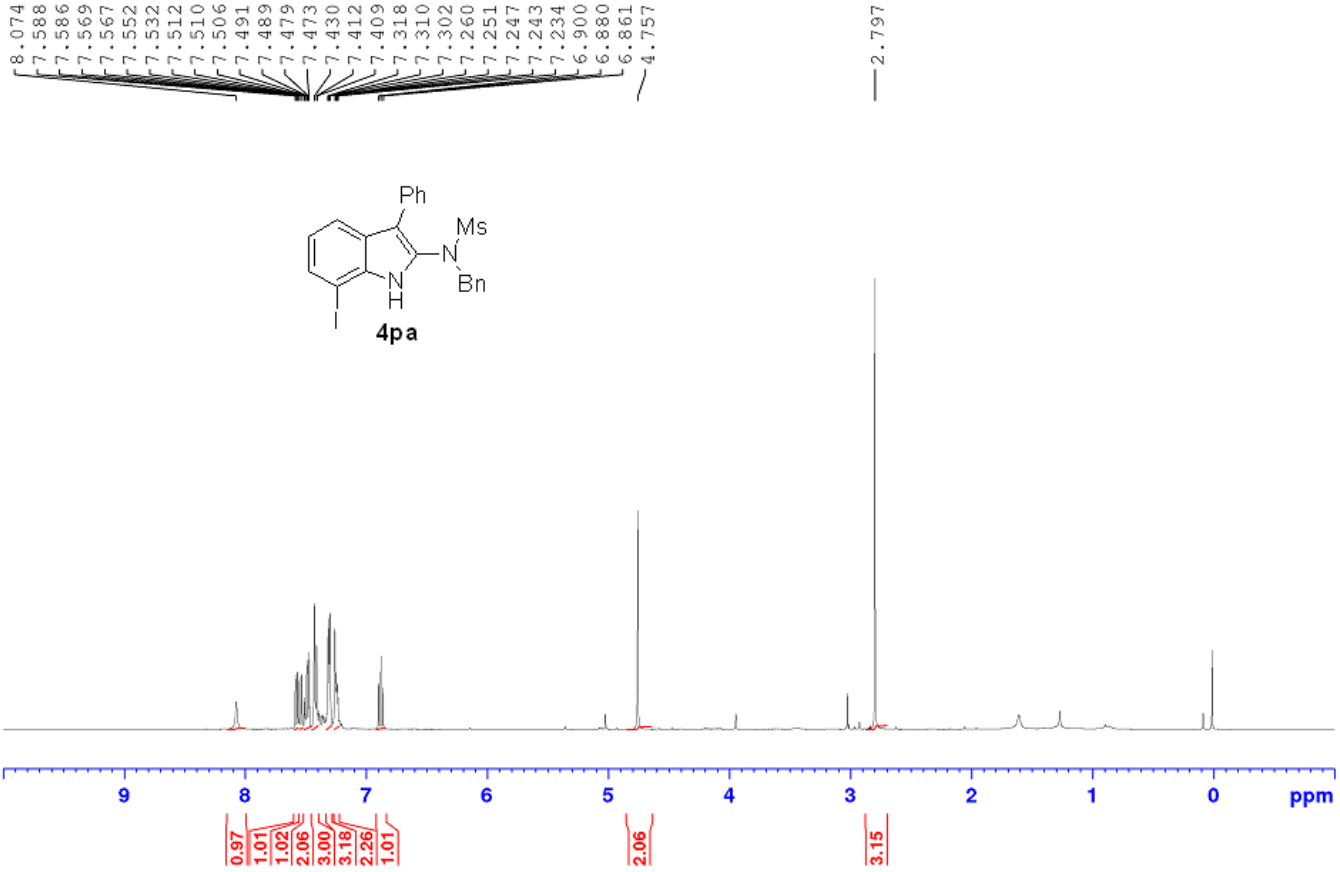


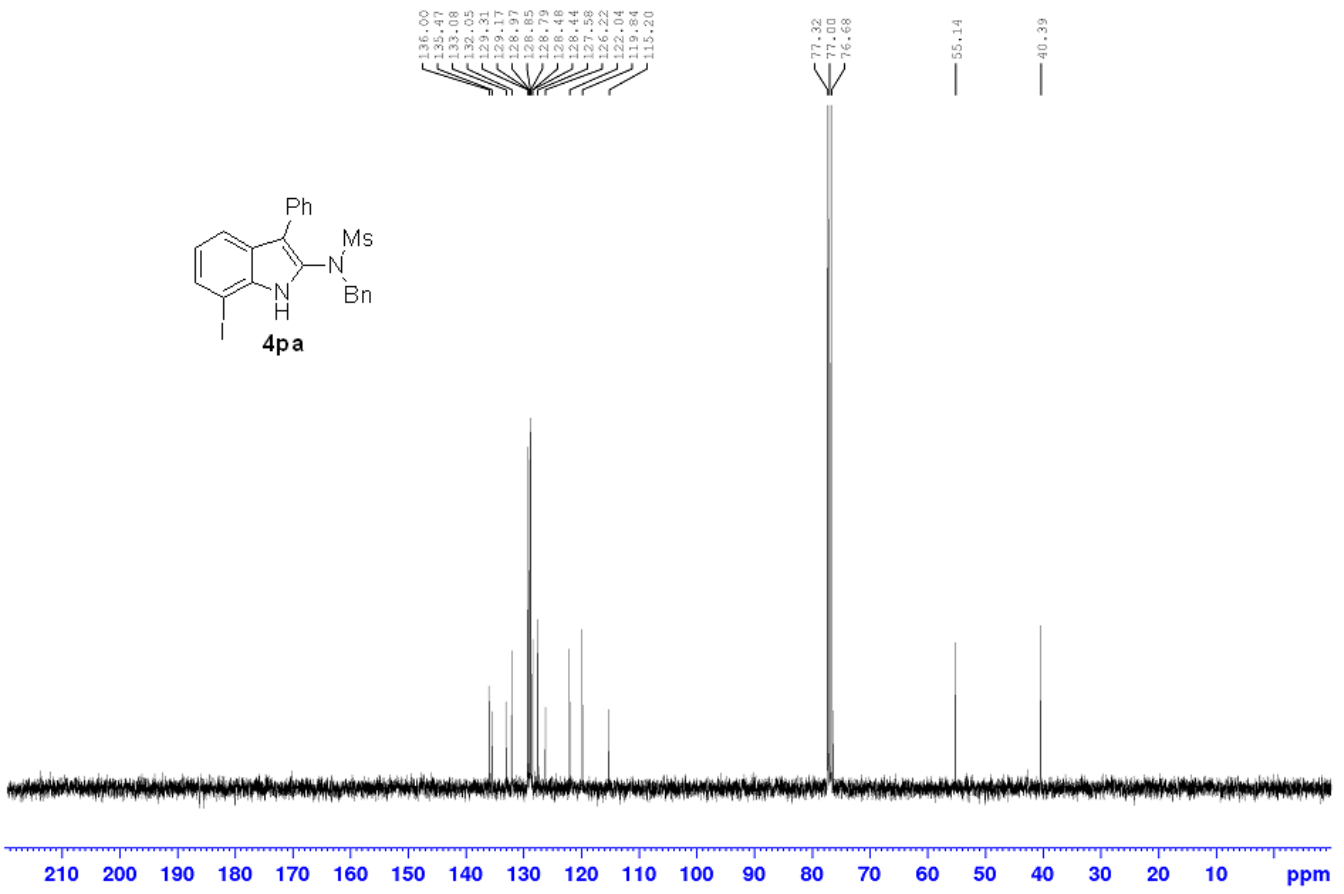
_N_-Benzyl-_N_-(7-bromo-3-phenyl-1_H_-indol-2-yl)methanesulfonamide (4oa)



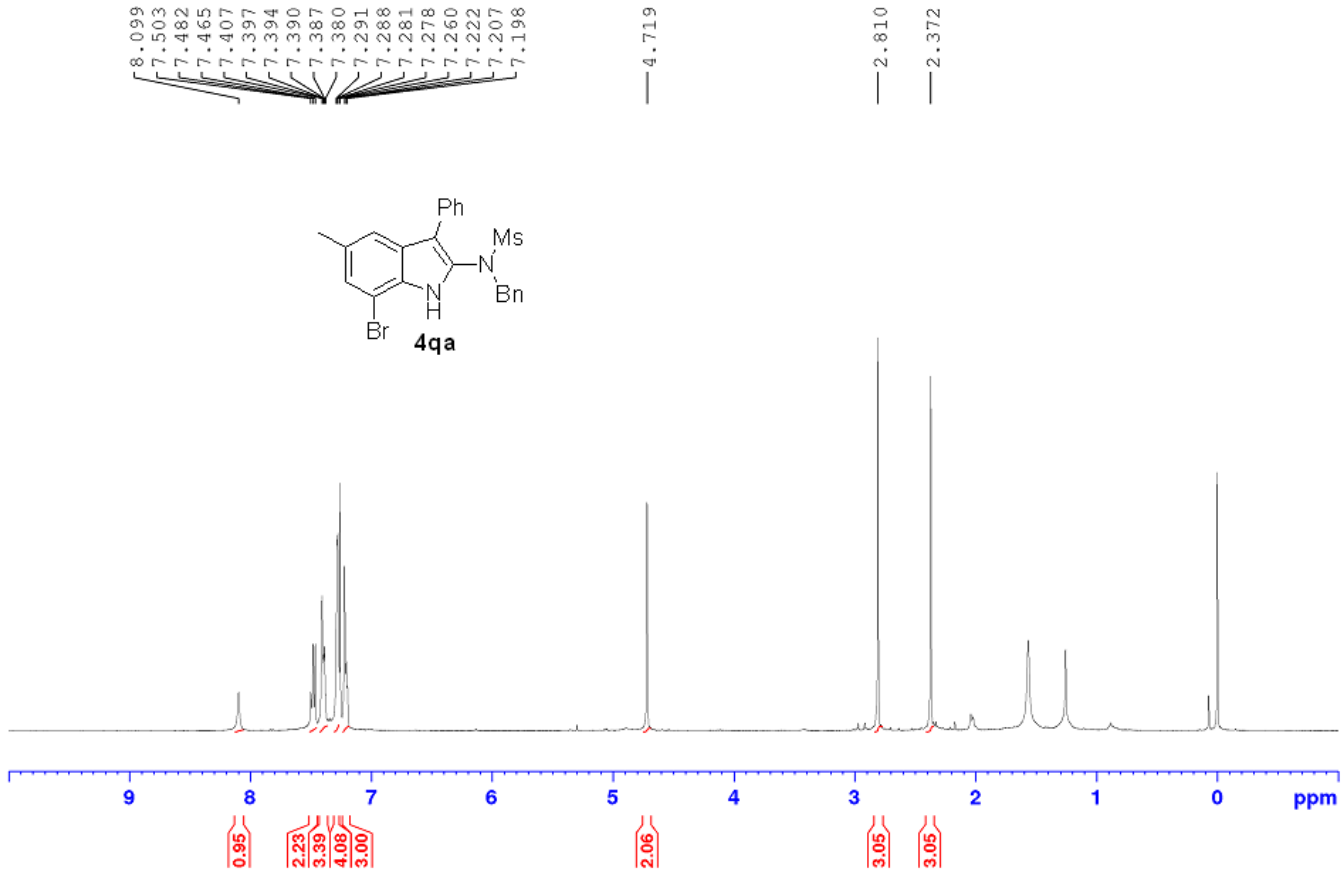


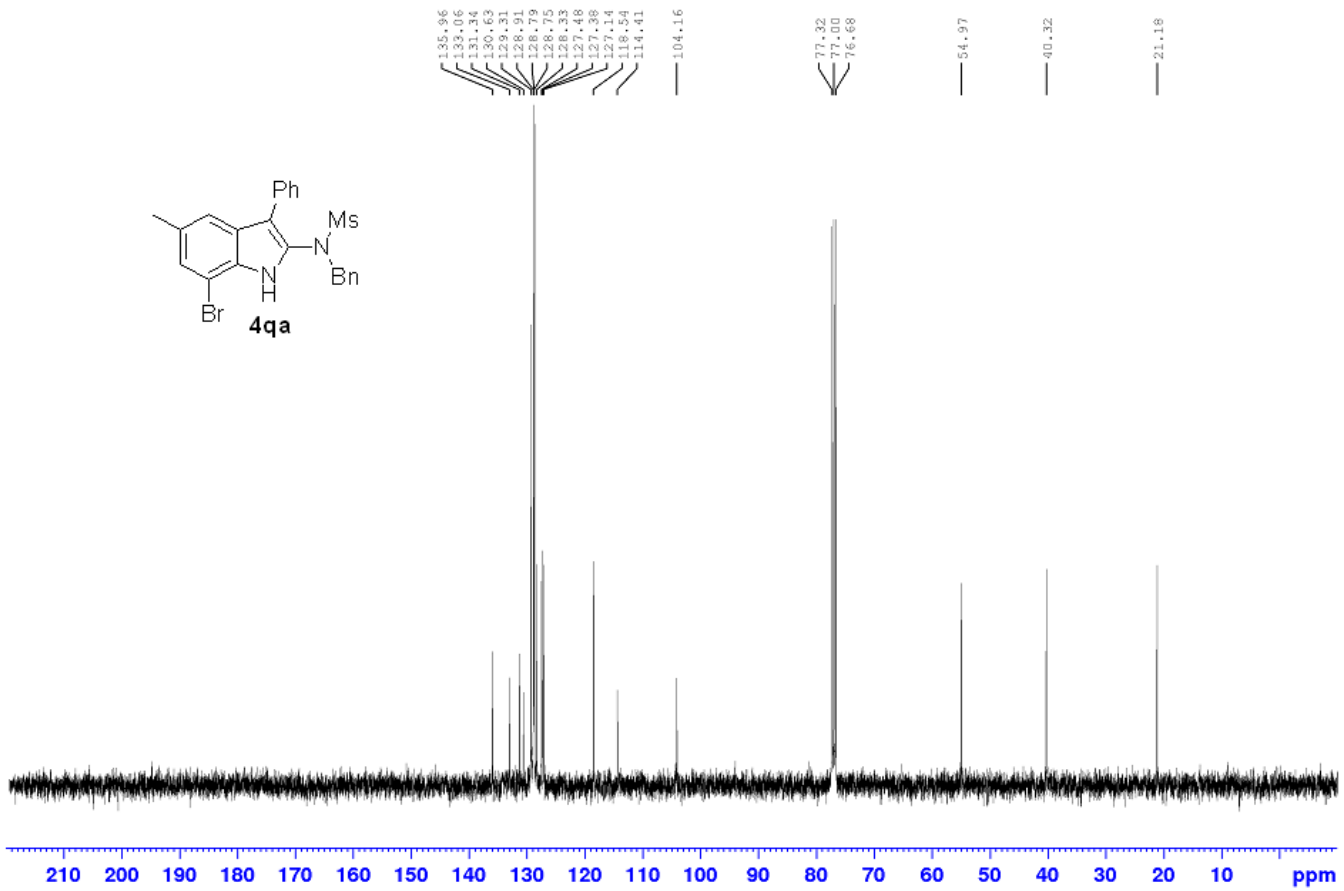
_N_-Benzyl-_N_-(7-iodo-3-phenyl-1_H_-indol-2-yl)methanesulfonamide (4pa)



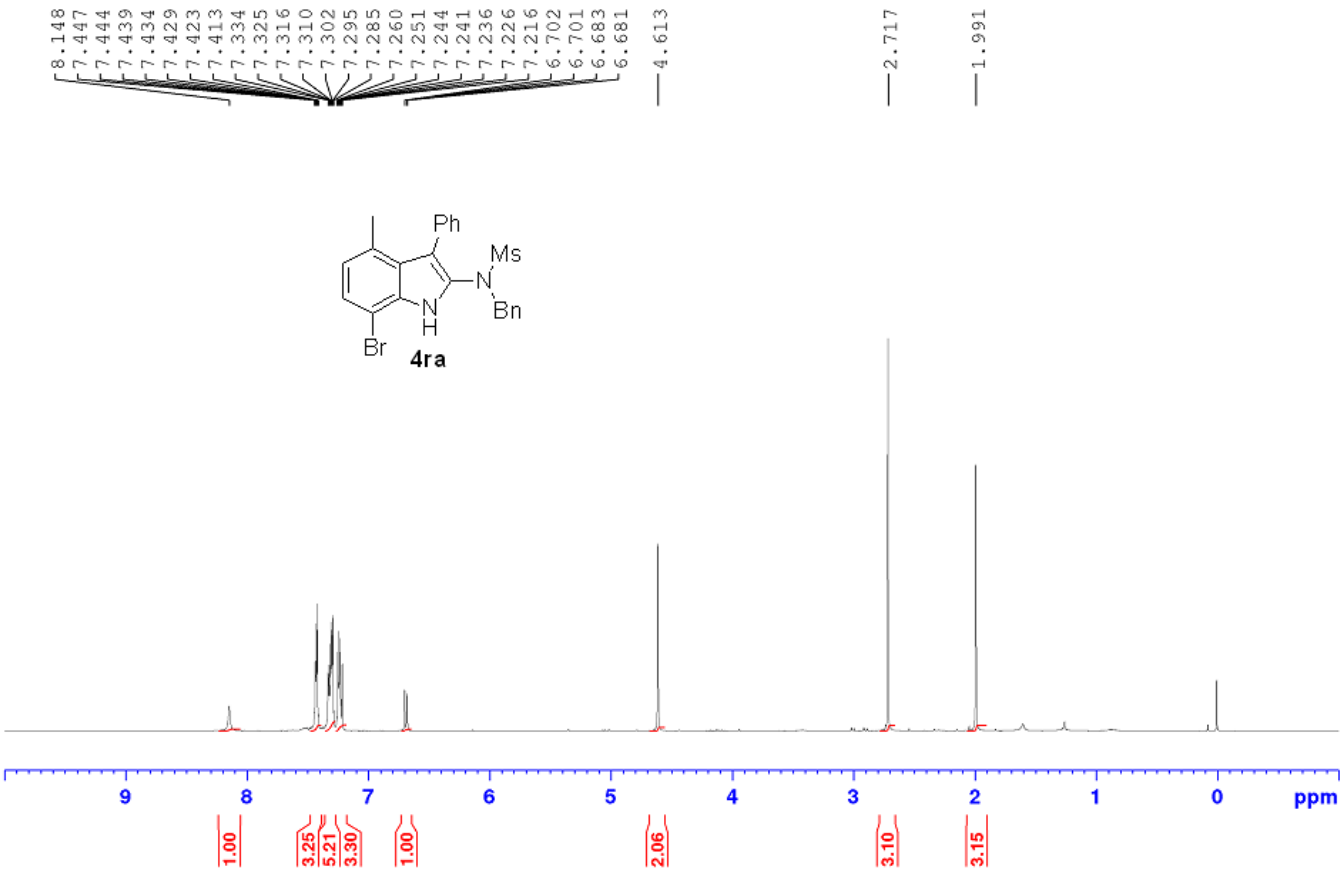


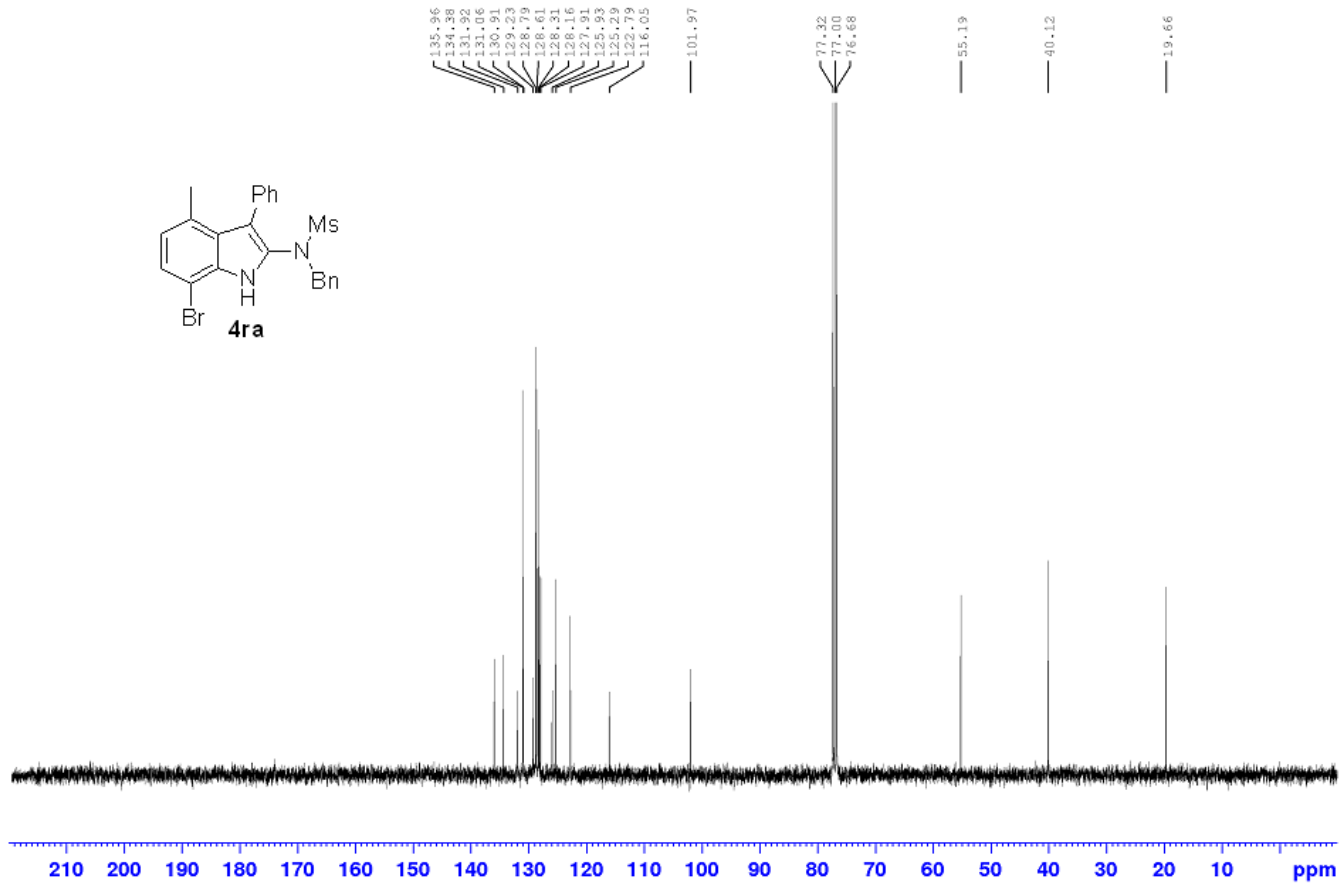
_N_-Benzyl-_N_-(7-bromo-5-methyl-3-phenyl-1_H_-indol-2-yl)methanesulfonamide (4qa)



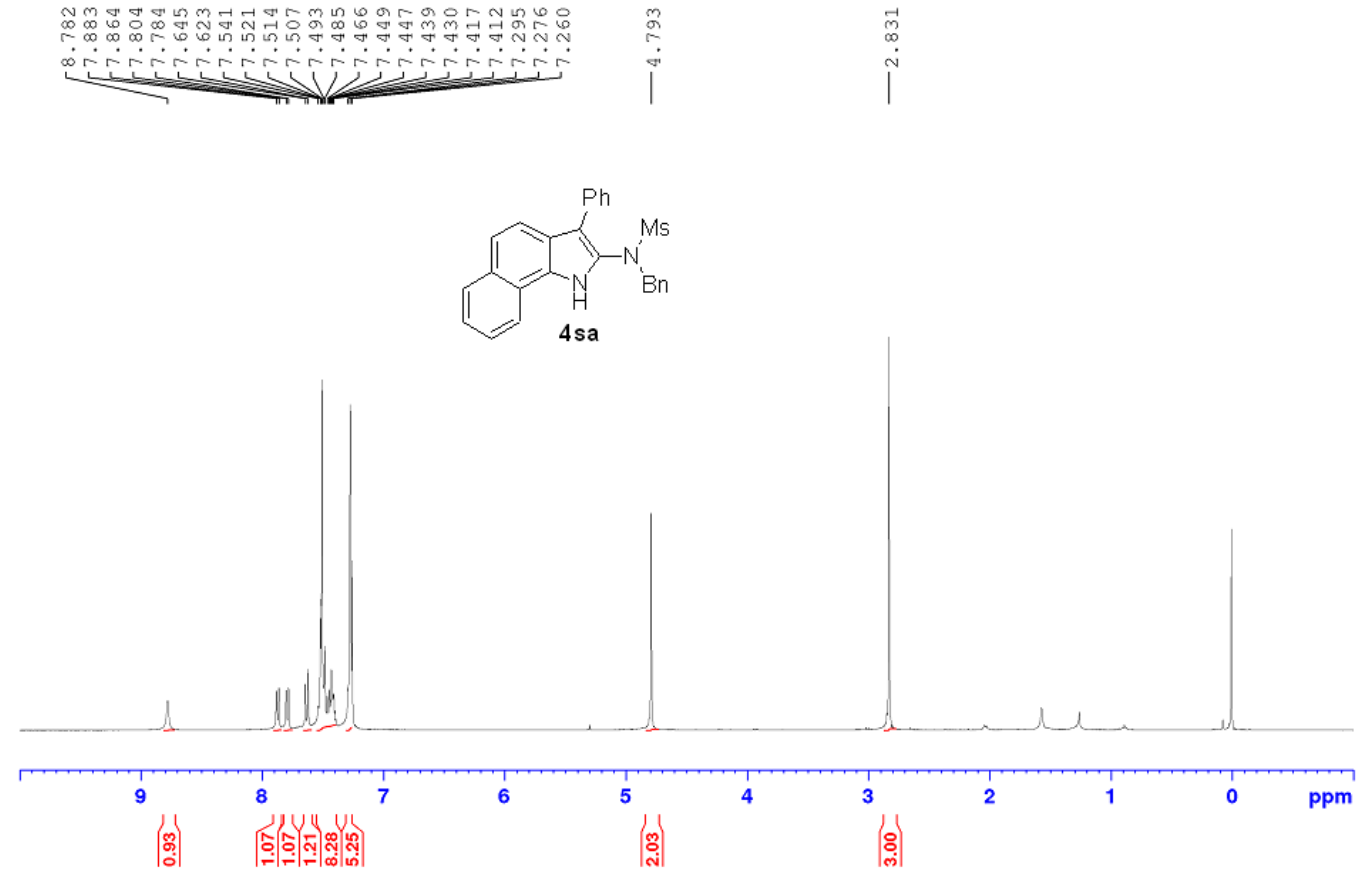


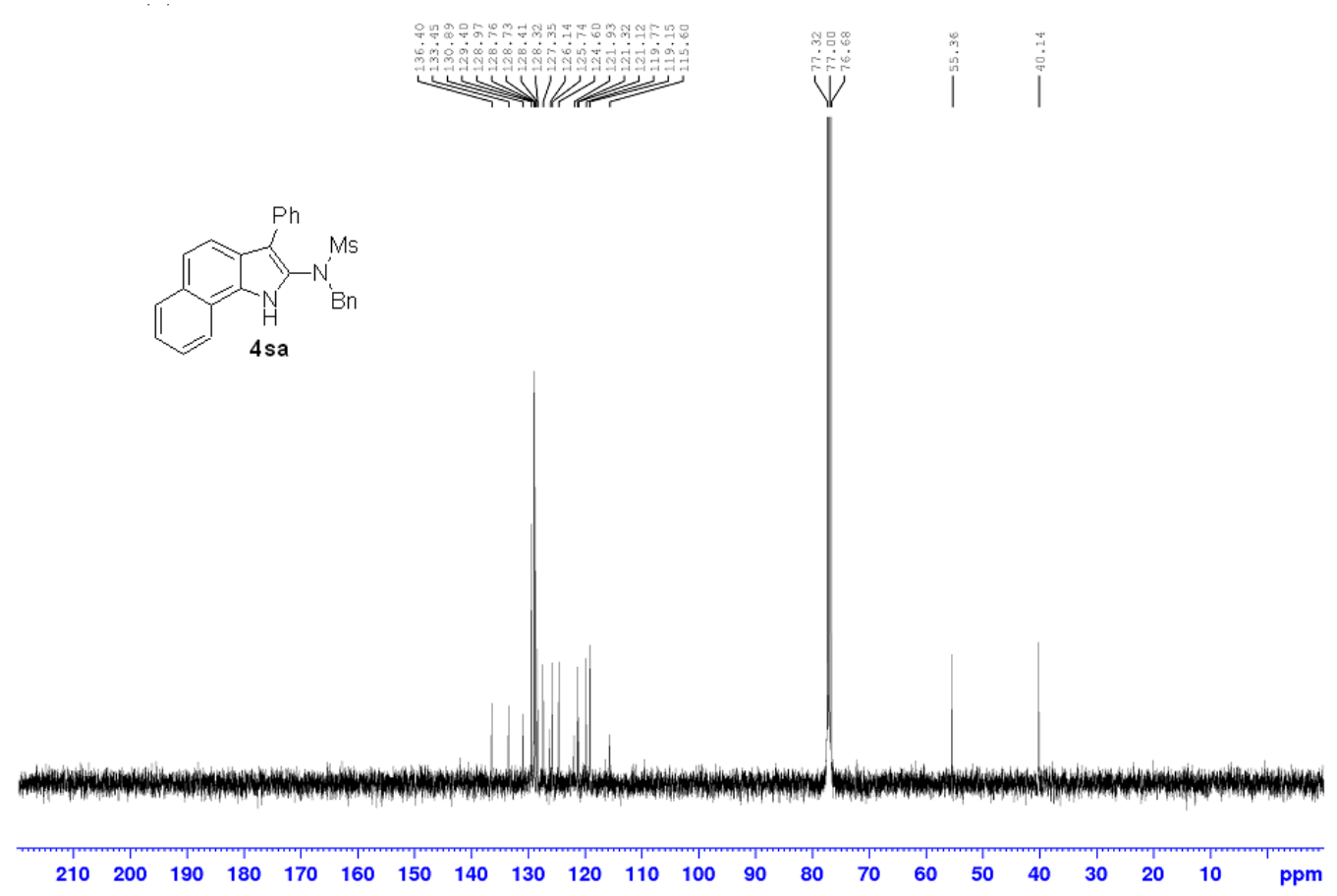
_N_-Benzyl-_N_-(7-bromo-4-methyl-3-phenyl-1_H_-indol-2-yl)methanesulfonamide (4ra)



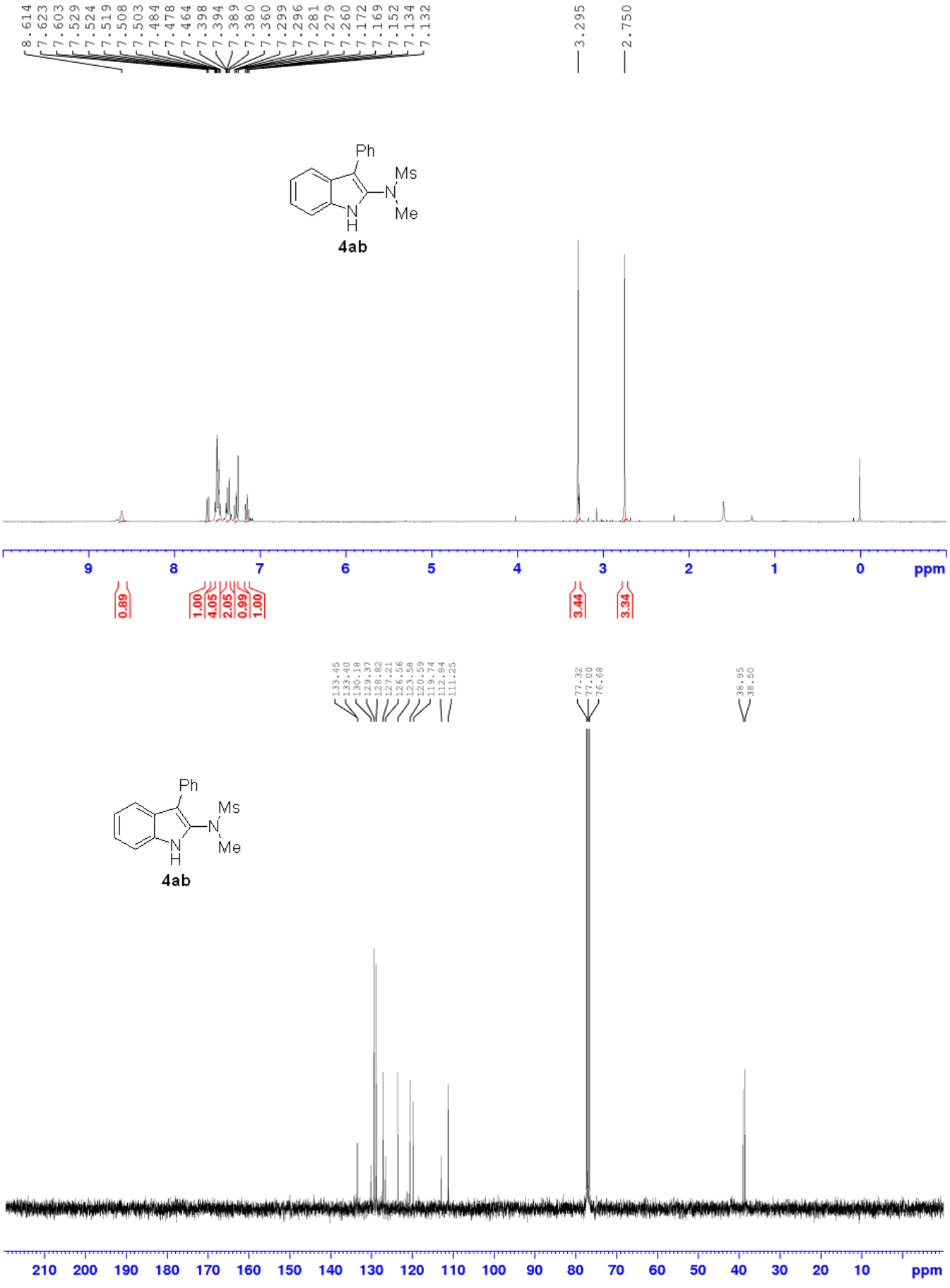


***N*-Benzyl-*N*-(3-phenyl-1*H*-benzo[*g*]indol-2-yl)methanesulfonamide (4sa)**

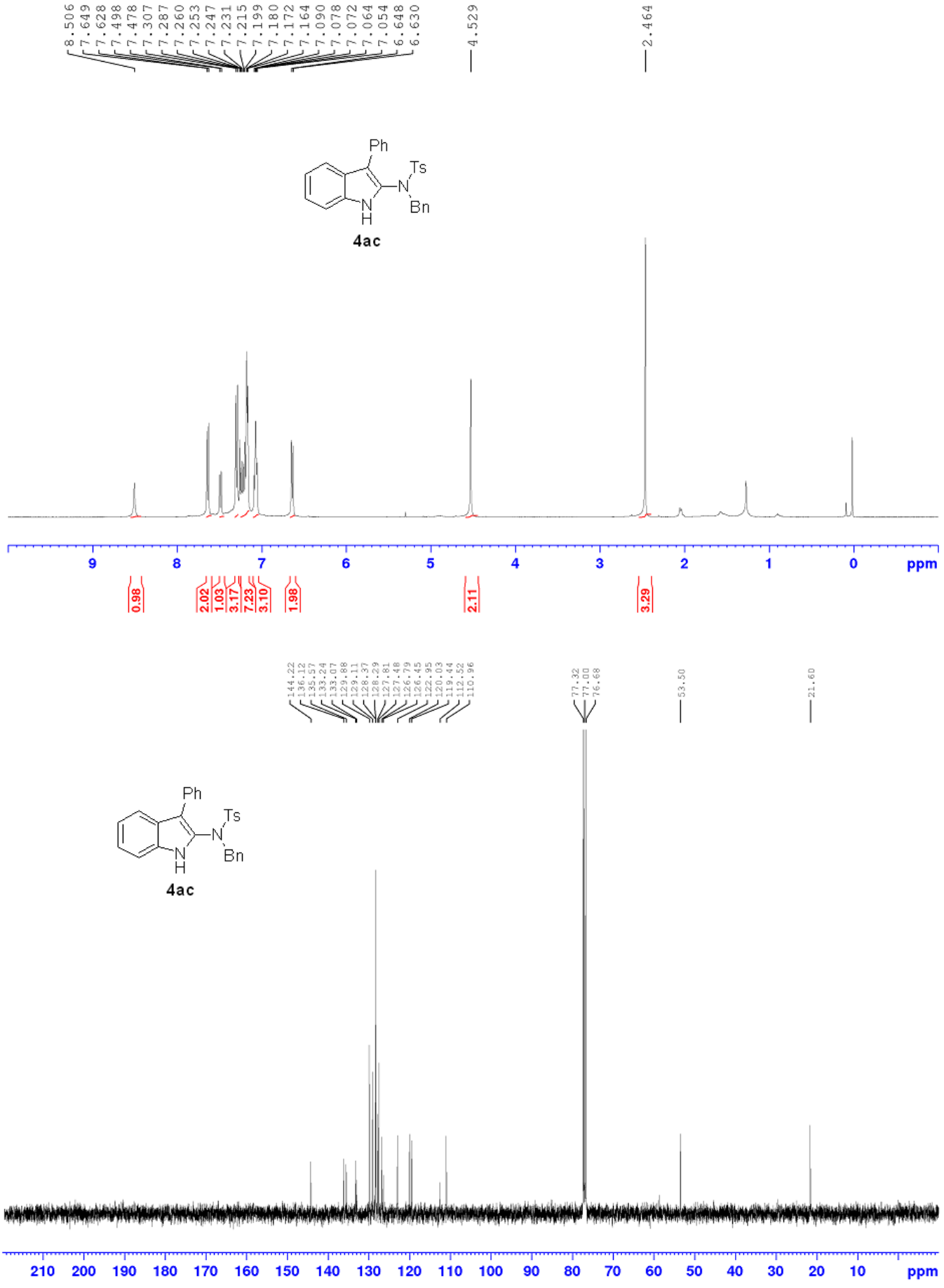




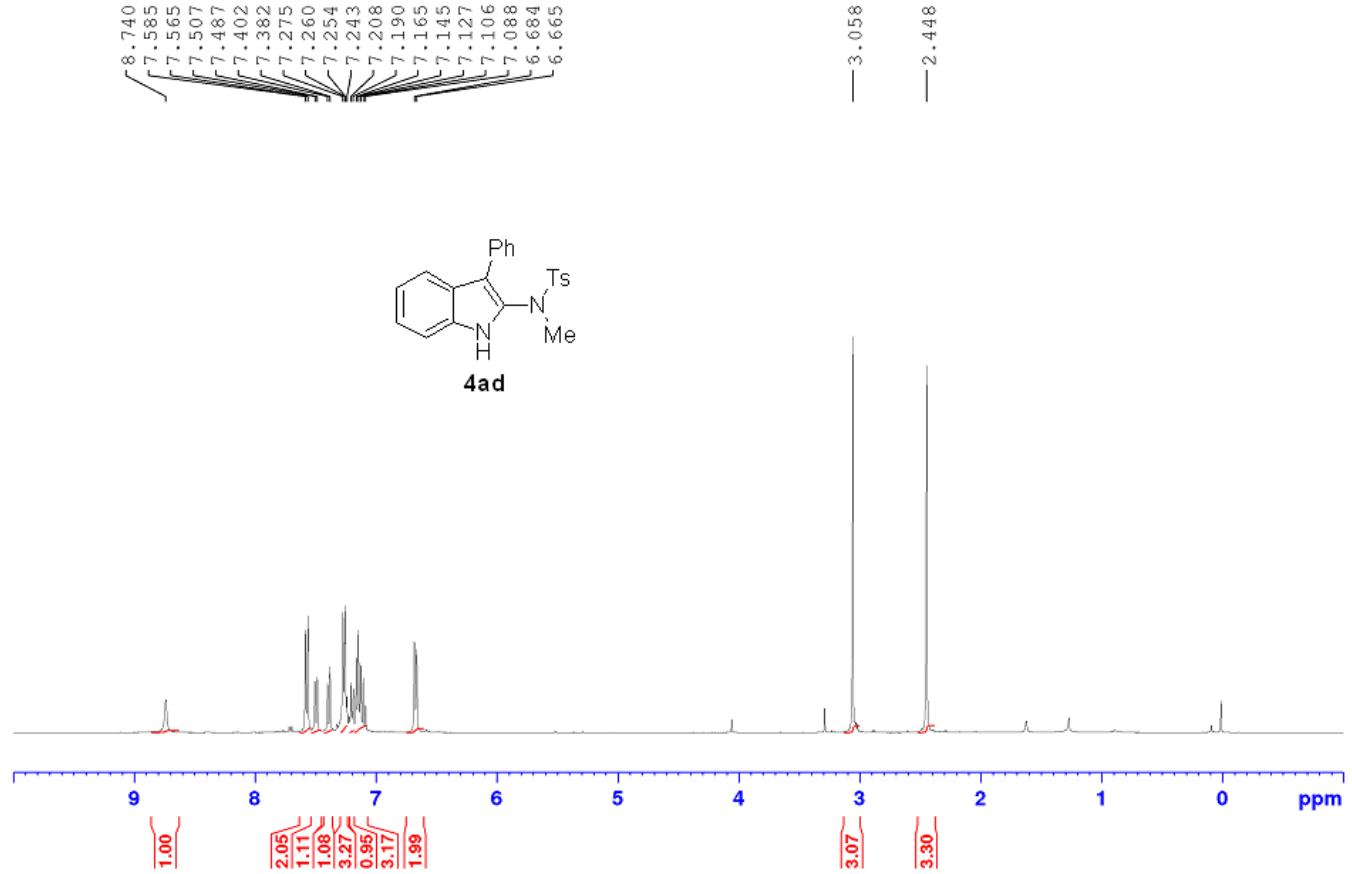
_N_-Methyl-_N_-(3-phenyl-1_H_-indol-2-yl)methanesulfonamide (4ab)

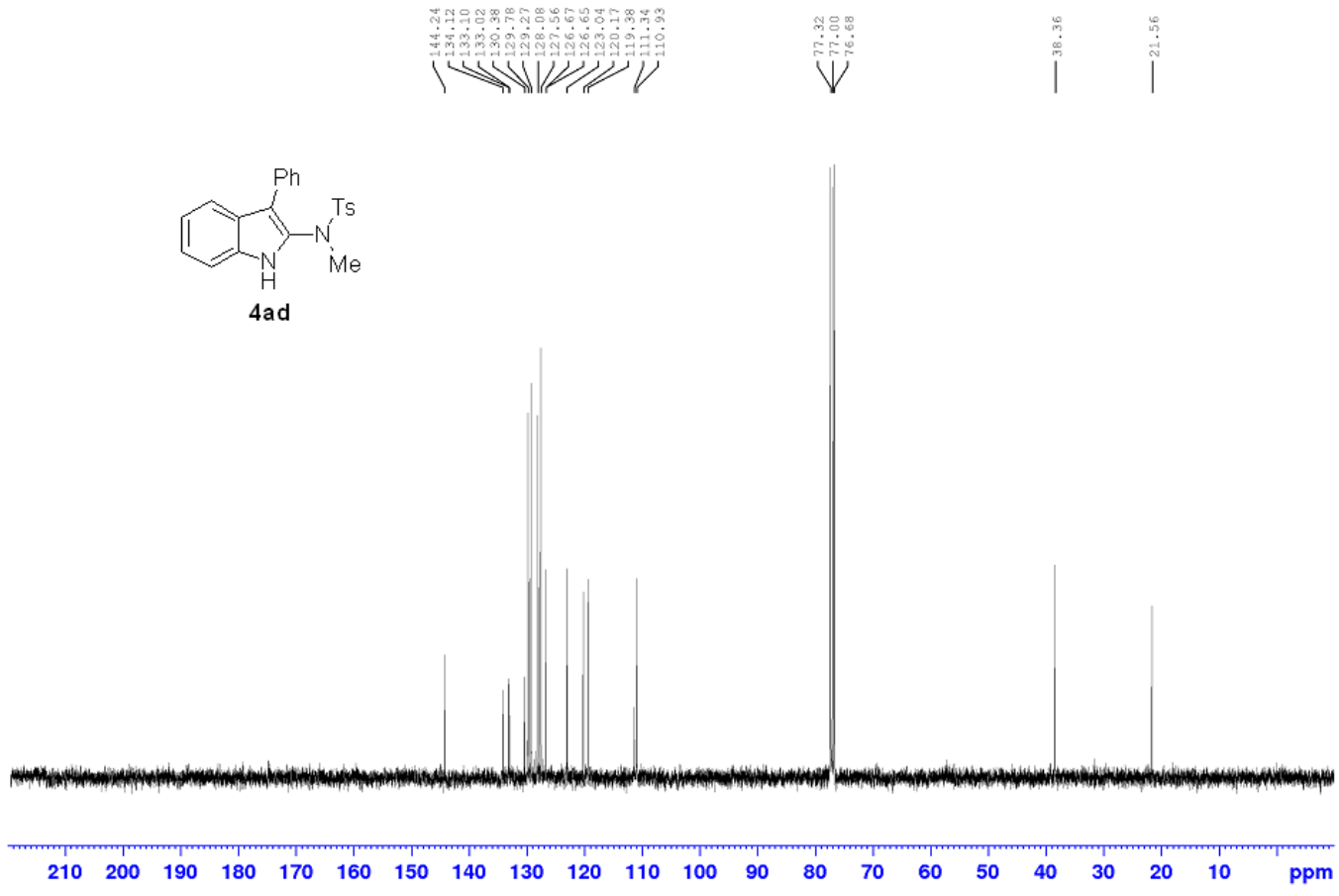


_N_-Benzyl-4-methyl-_N_-(3-phenyl-1_H_-indol-2-yl)benzenesulfonamide (4ac)

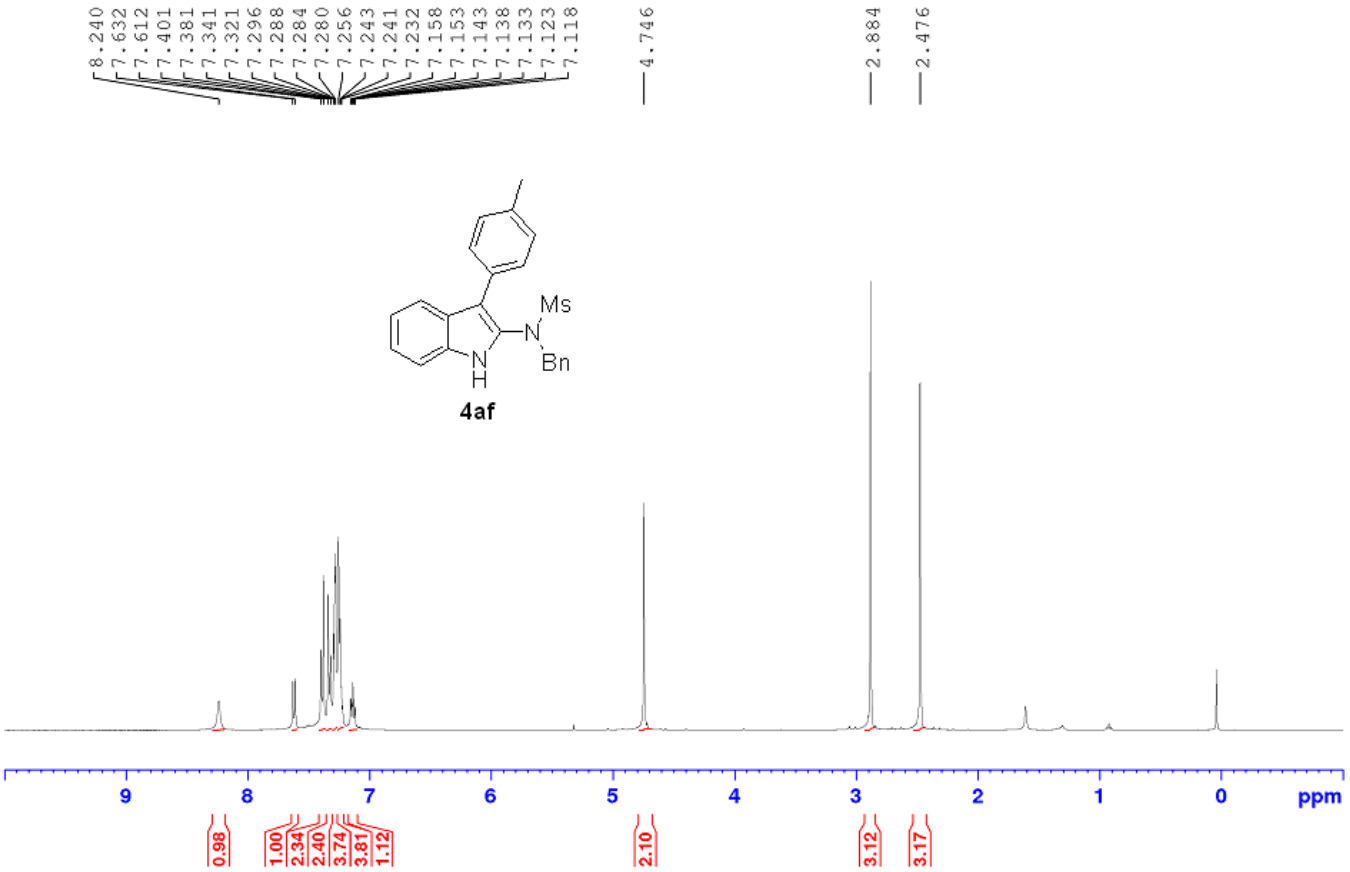


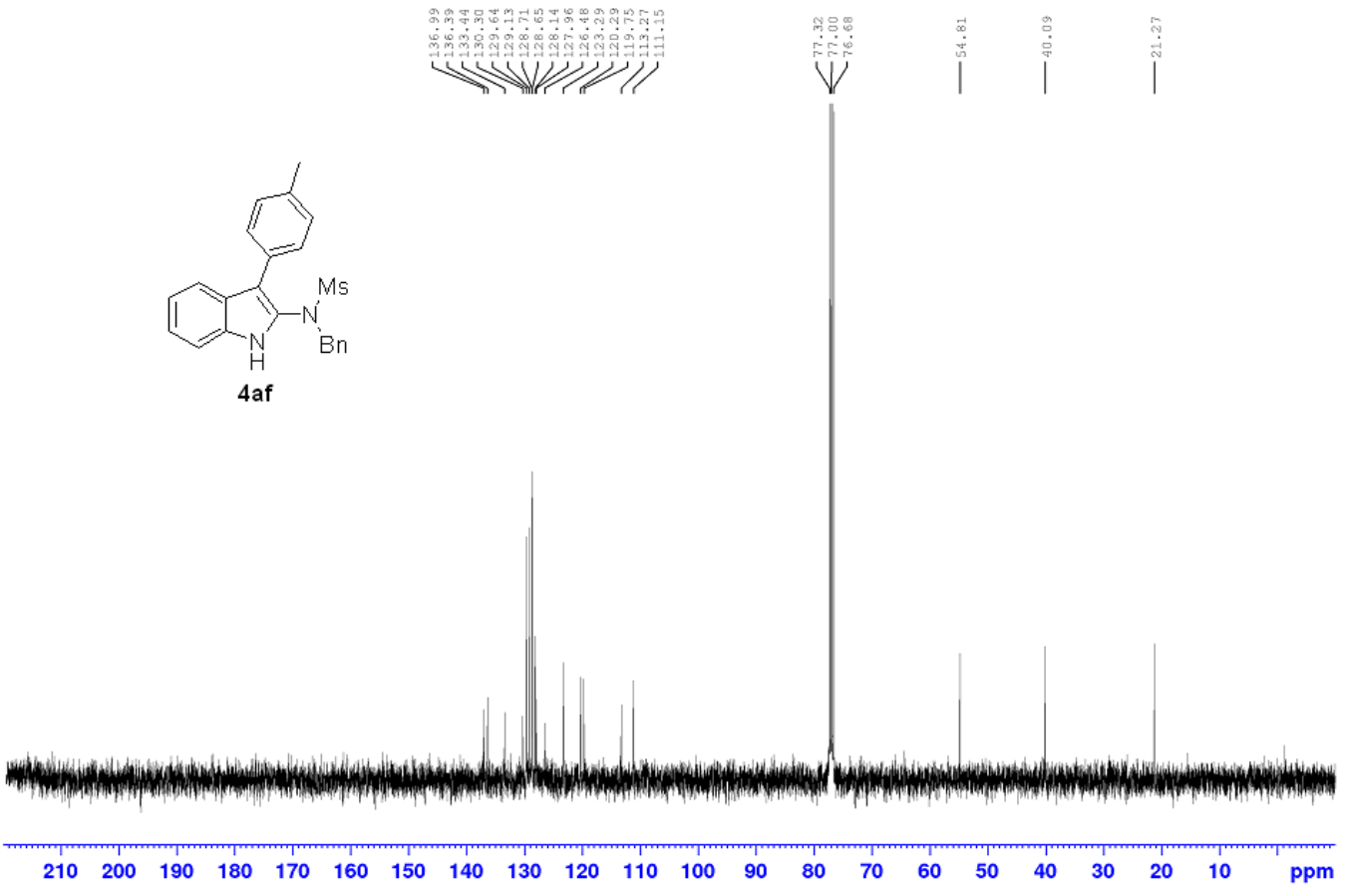
_N_,4-Dimethyl-_N_-(3-phenyl-1_H_-indol-2-yl)benzenesulfonamide (4ad)



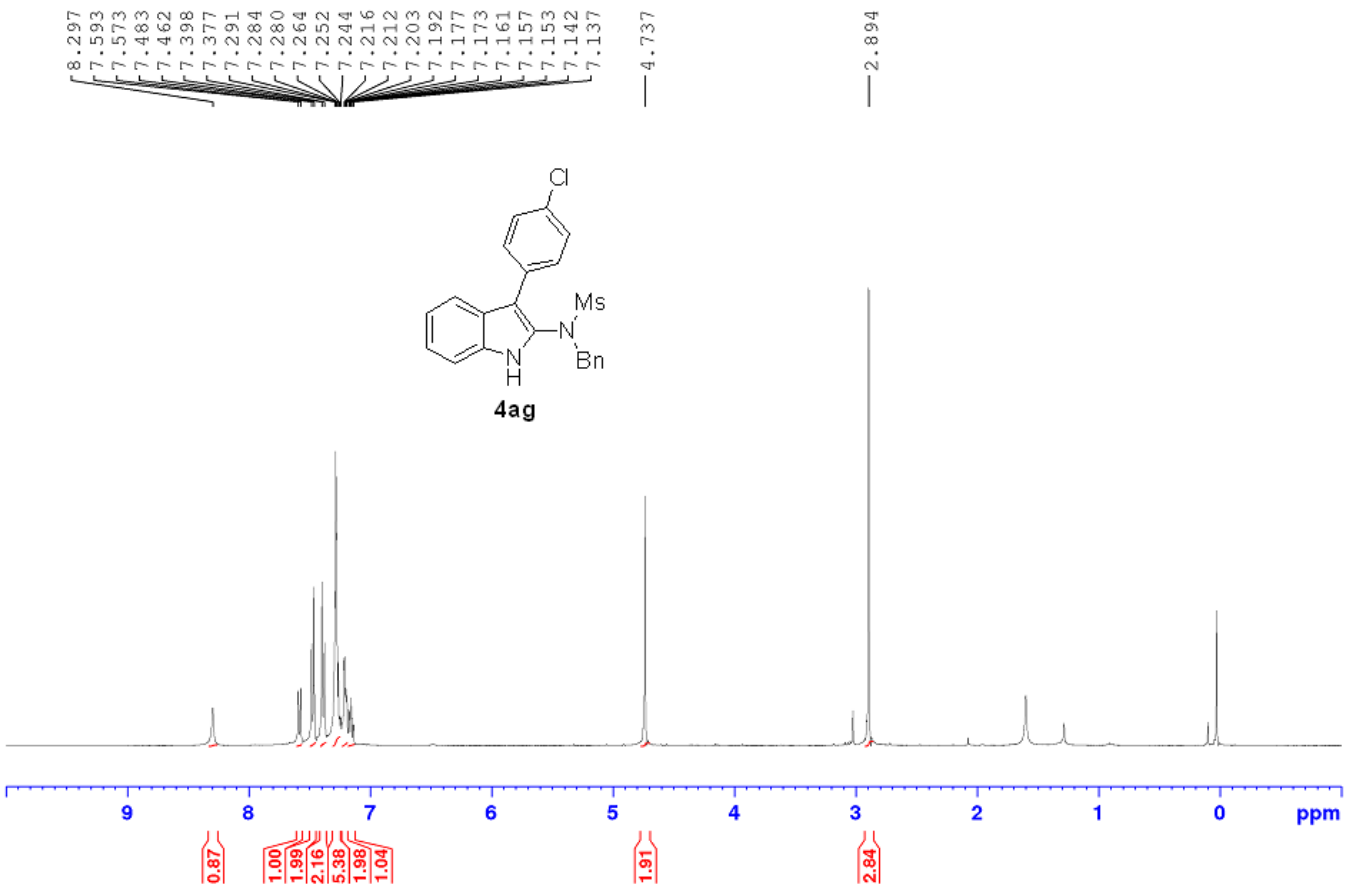


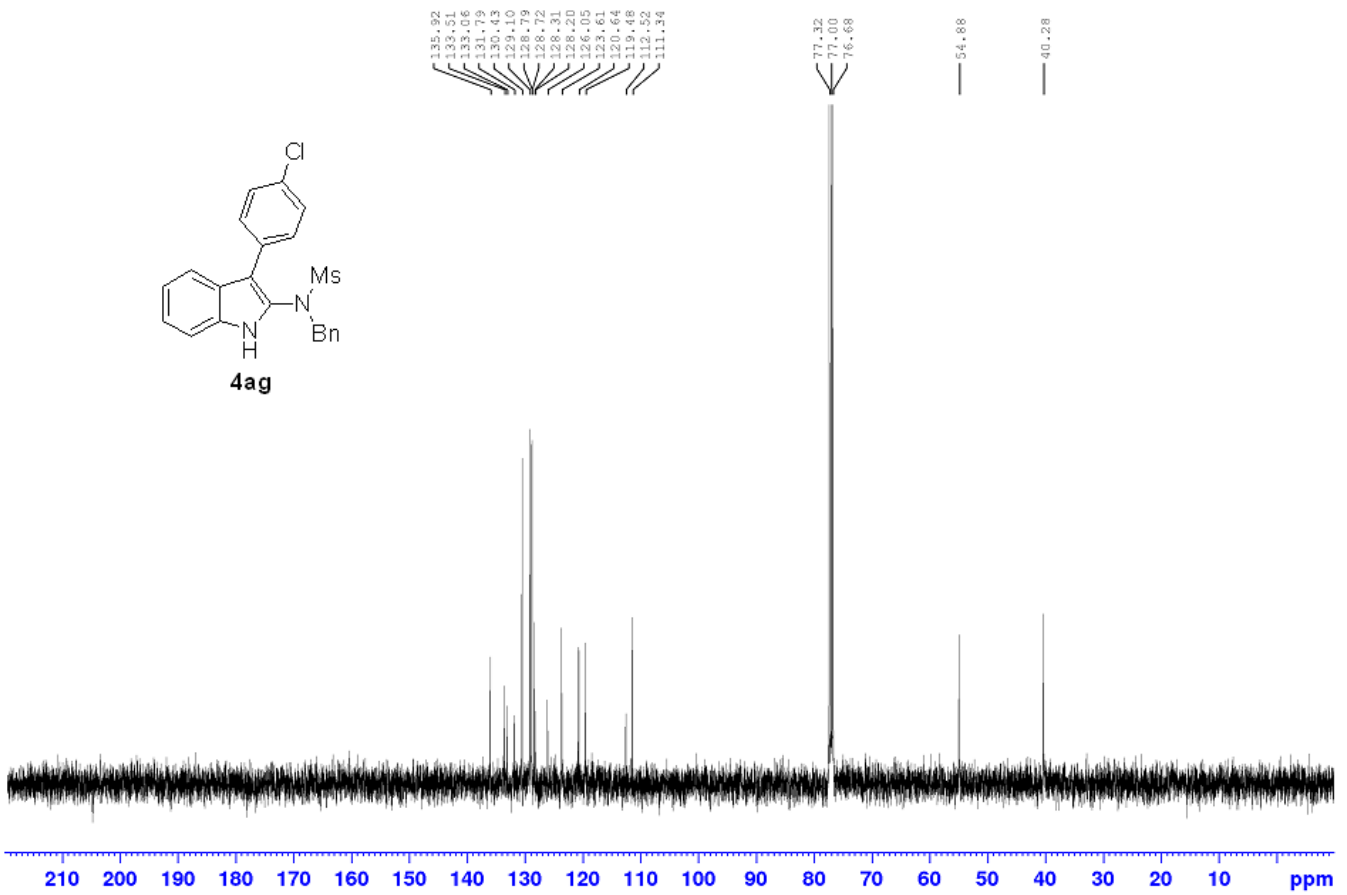
_N_-Benzyl-_N_-(3-(_p_-tolyl)-1_H_-indol-2-yl)methanesulfonamide (4af)



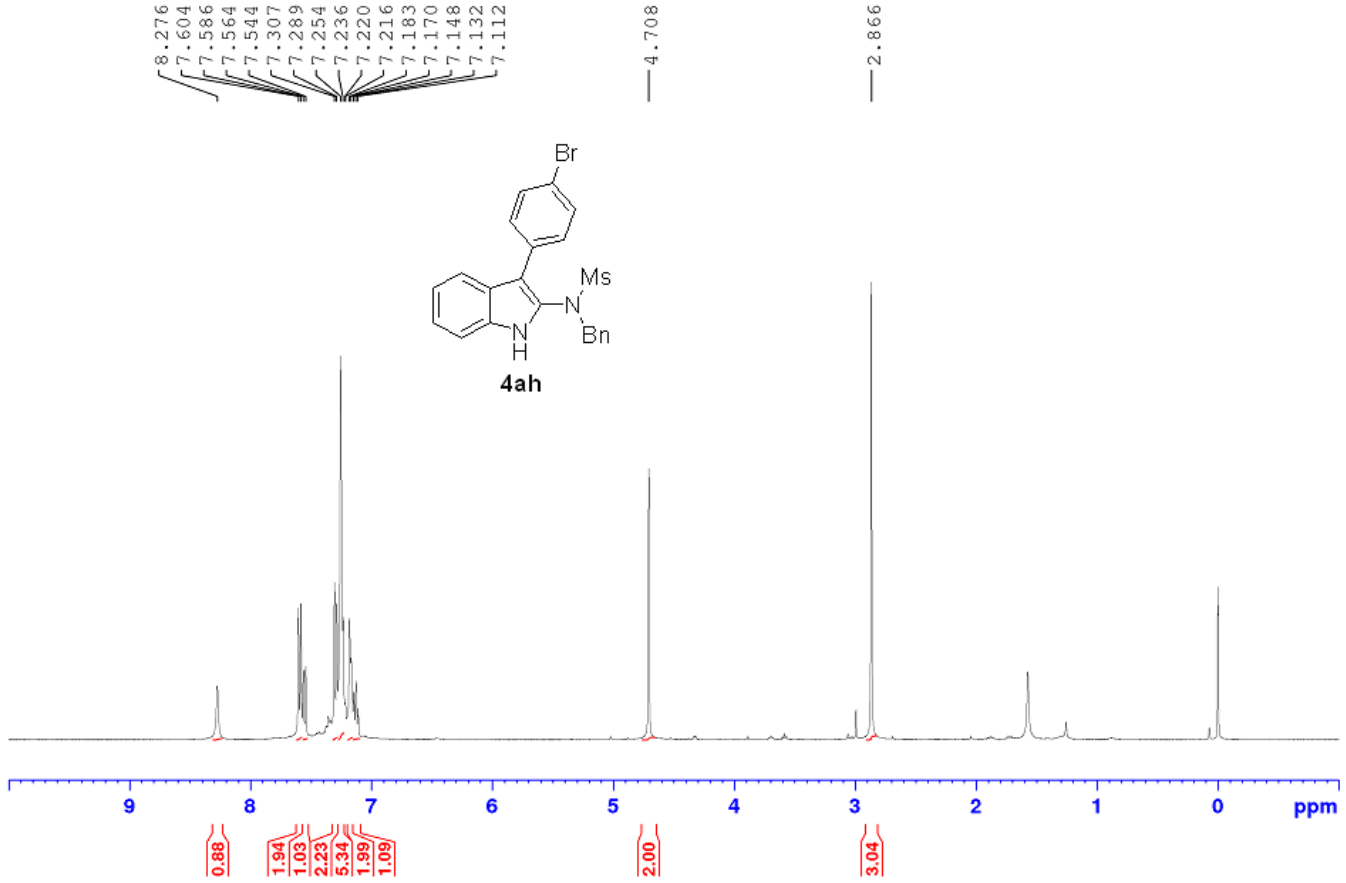


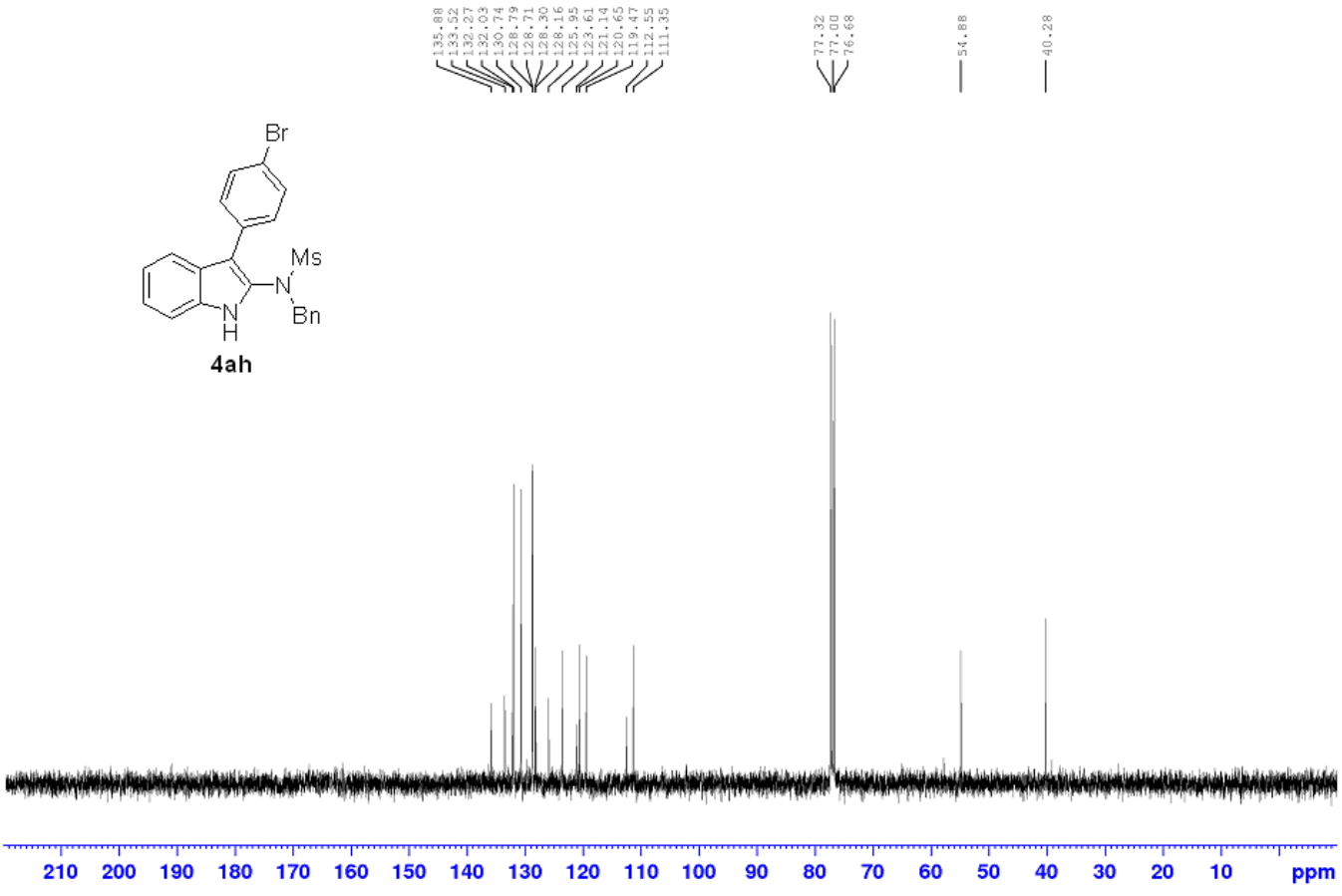
_N_-Benzyl-_N_-(3-(4-chlorophenyl)-1_H_-indol-2-yl)methanesulfonamide (4ag)



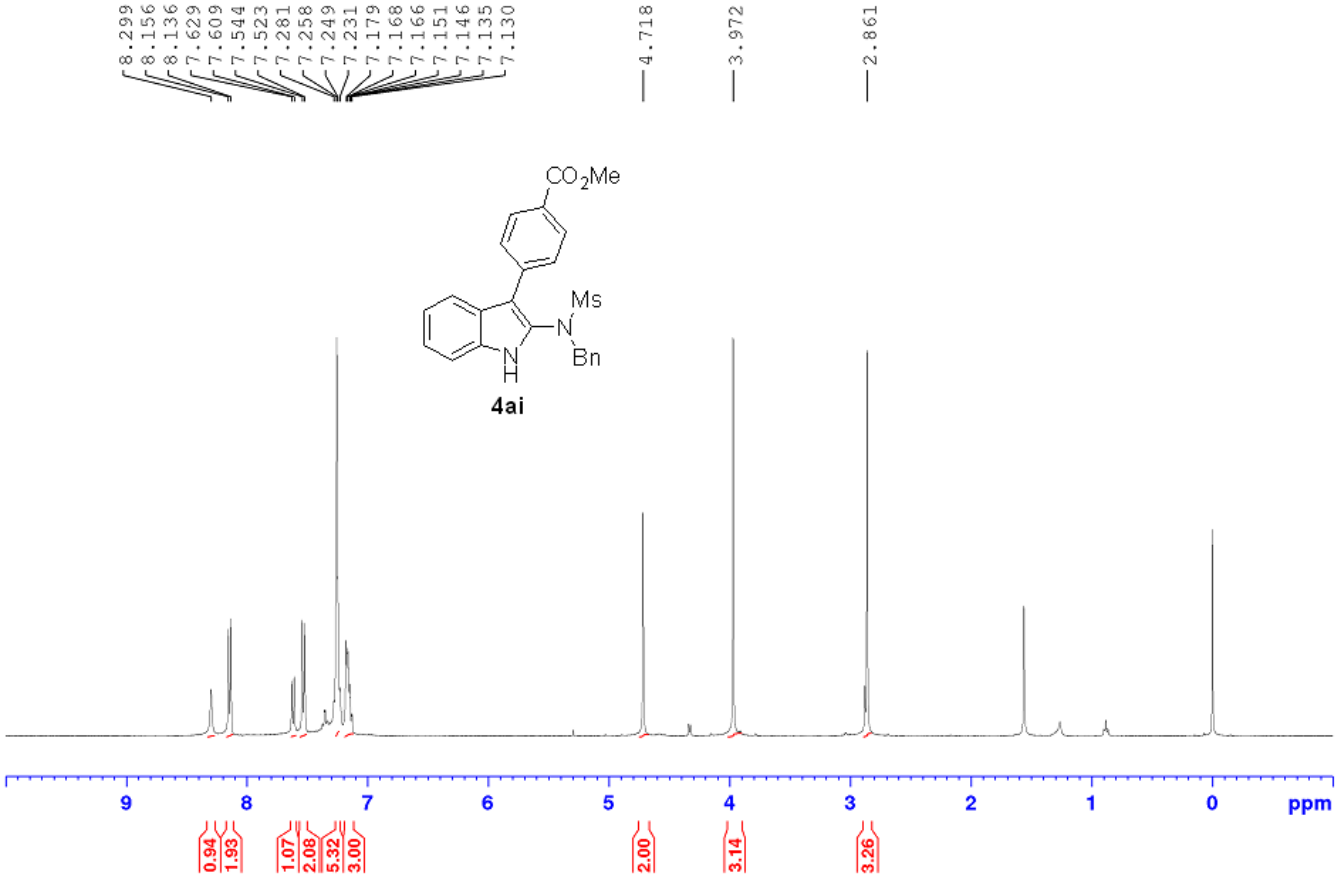


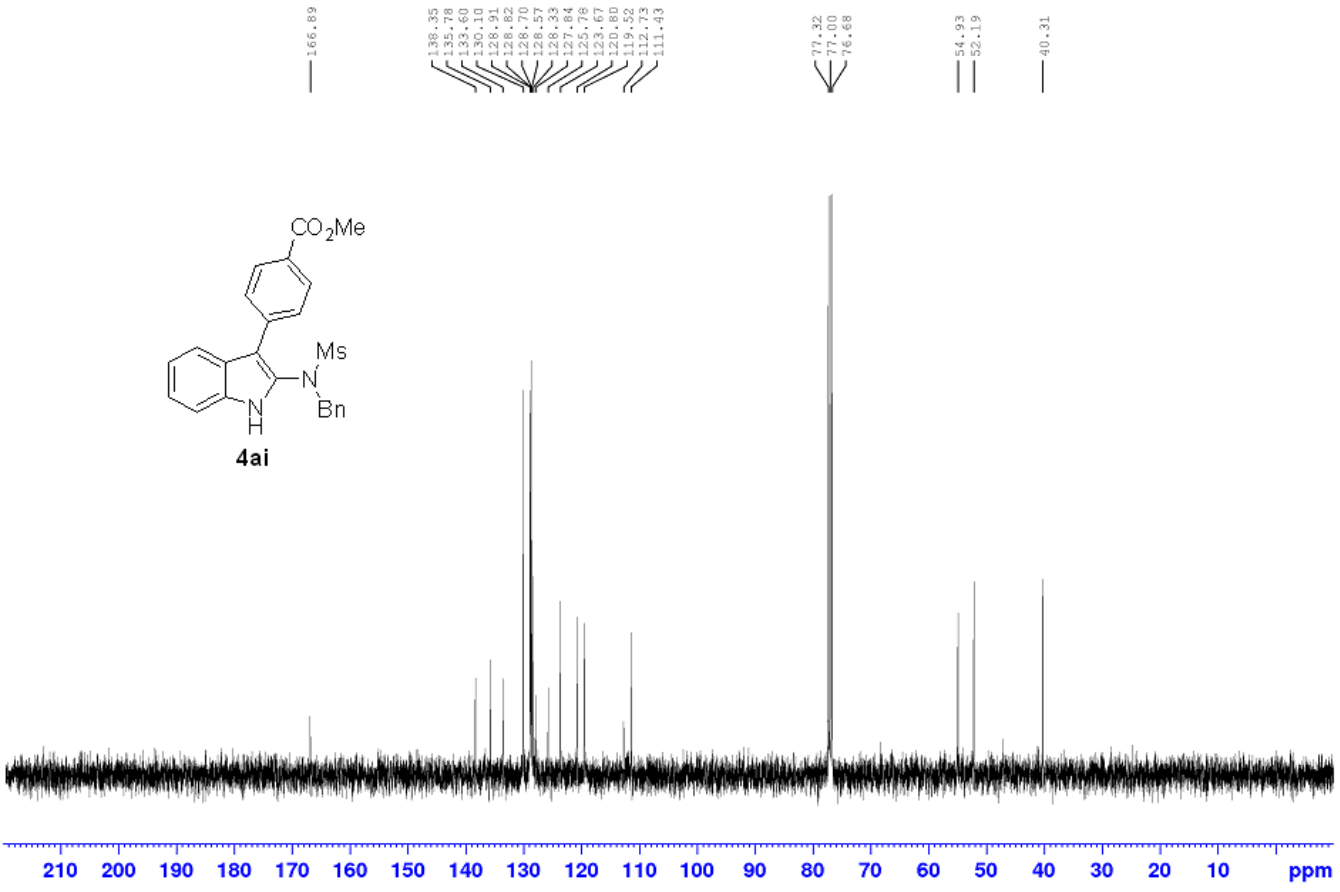
_N_-Benzyl-_N_-(3-(4-bromophenyl)-1_H_-indol-2-yl)methanesulfonamide (4ah)



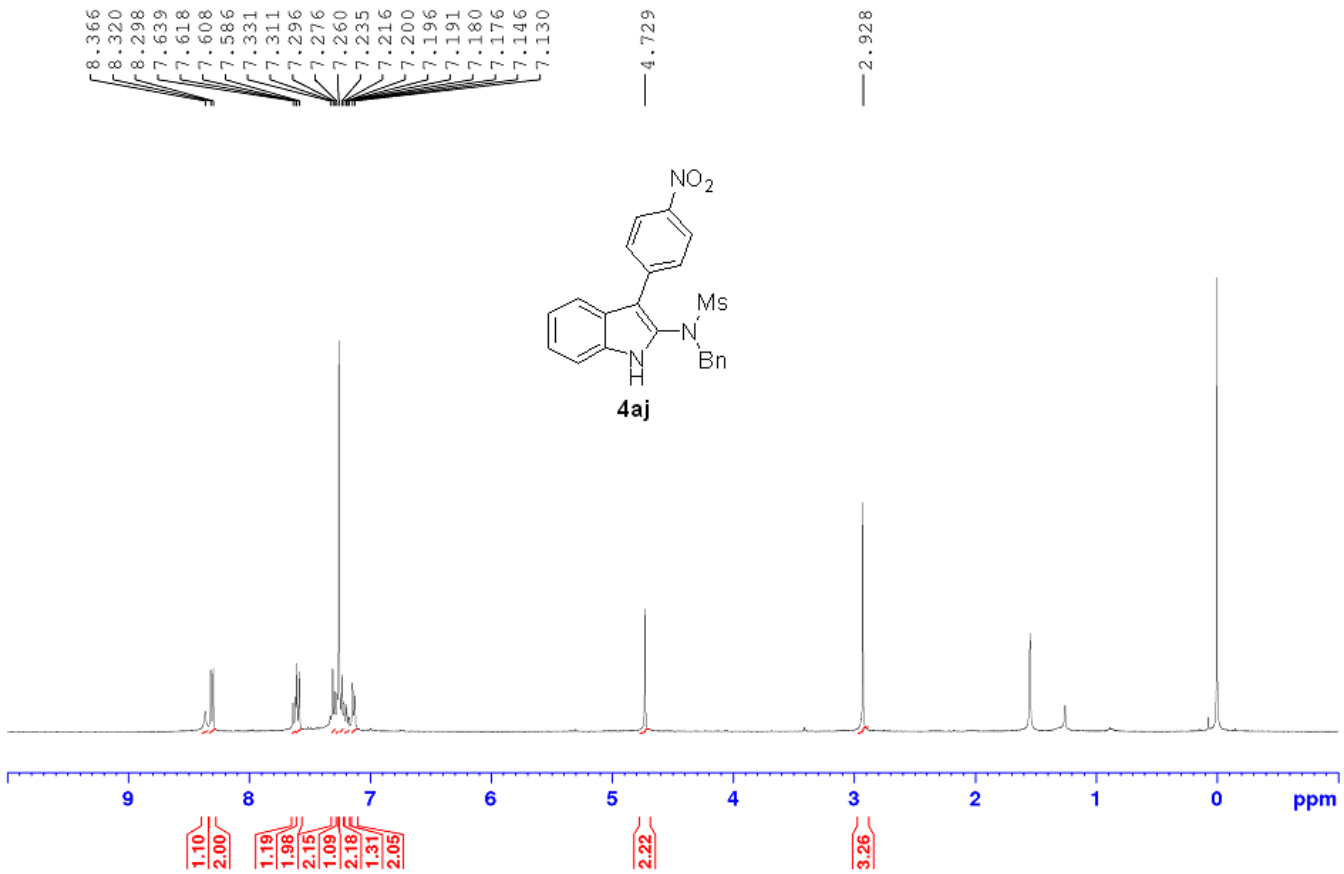


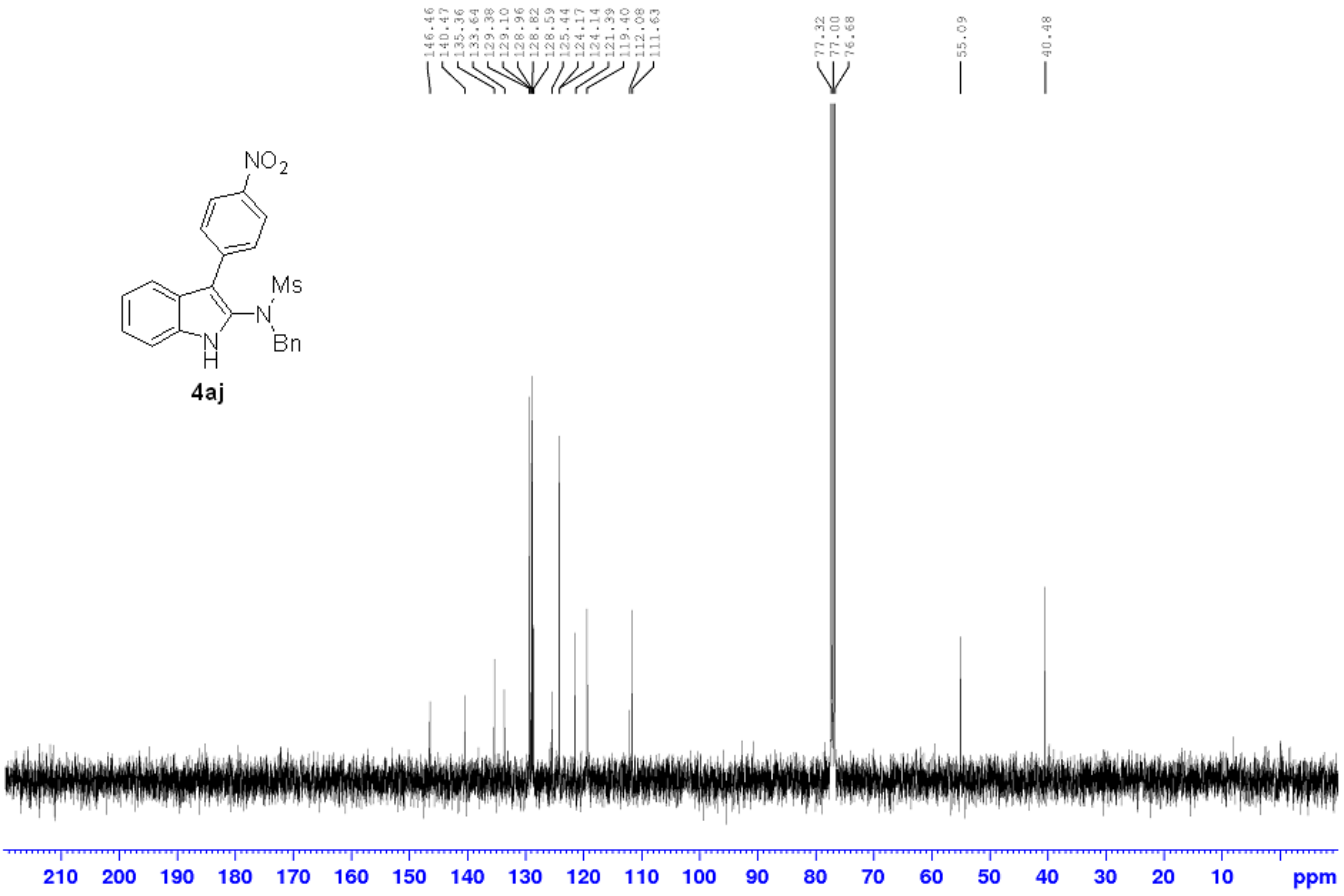
Methyl 4-(2-(*N*-Benzylmethylsulfonamido)-1*H*-indol-3-yl)benzoate (4ai)



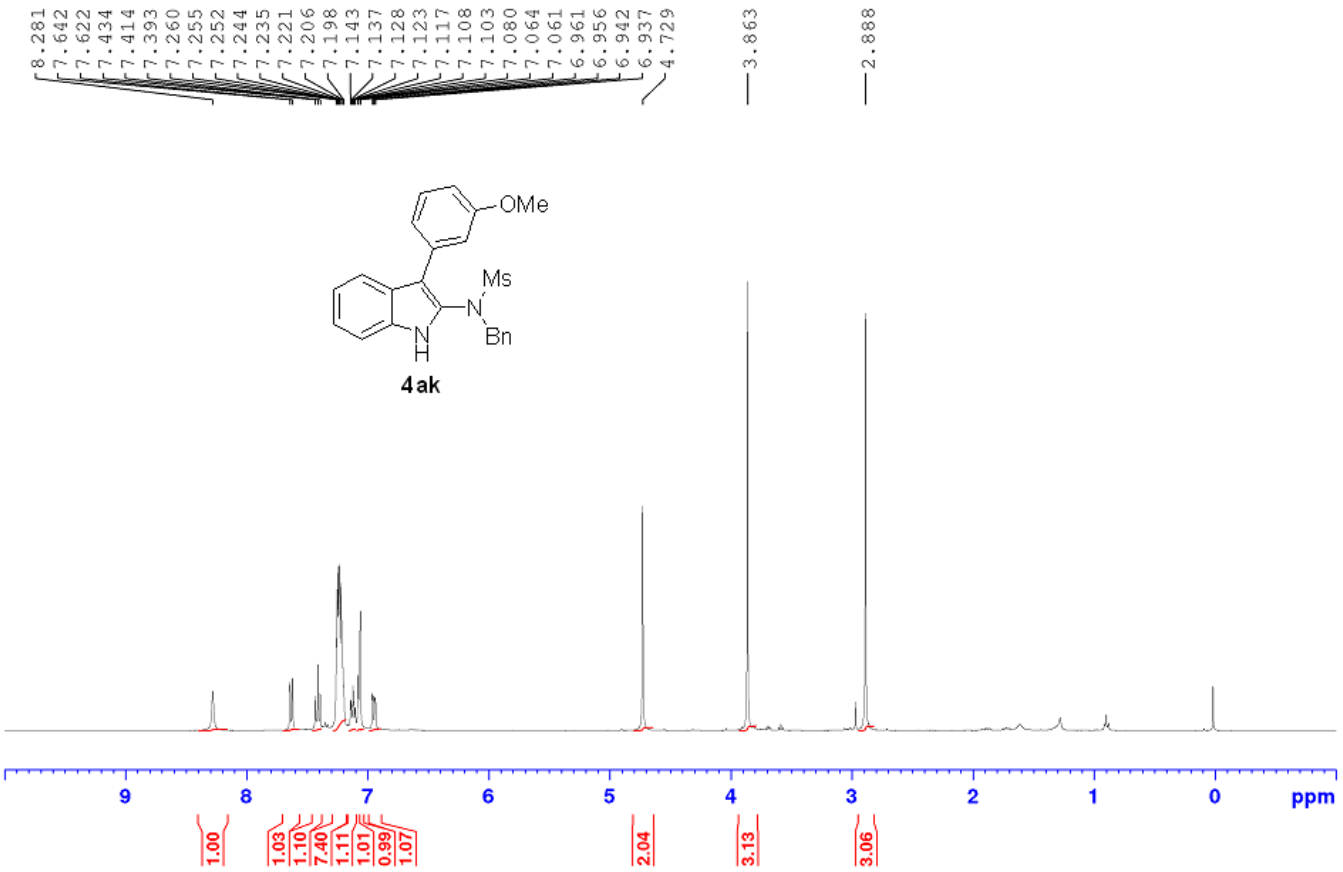


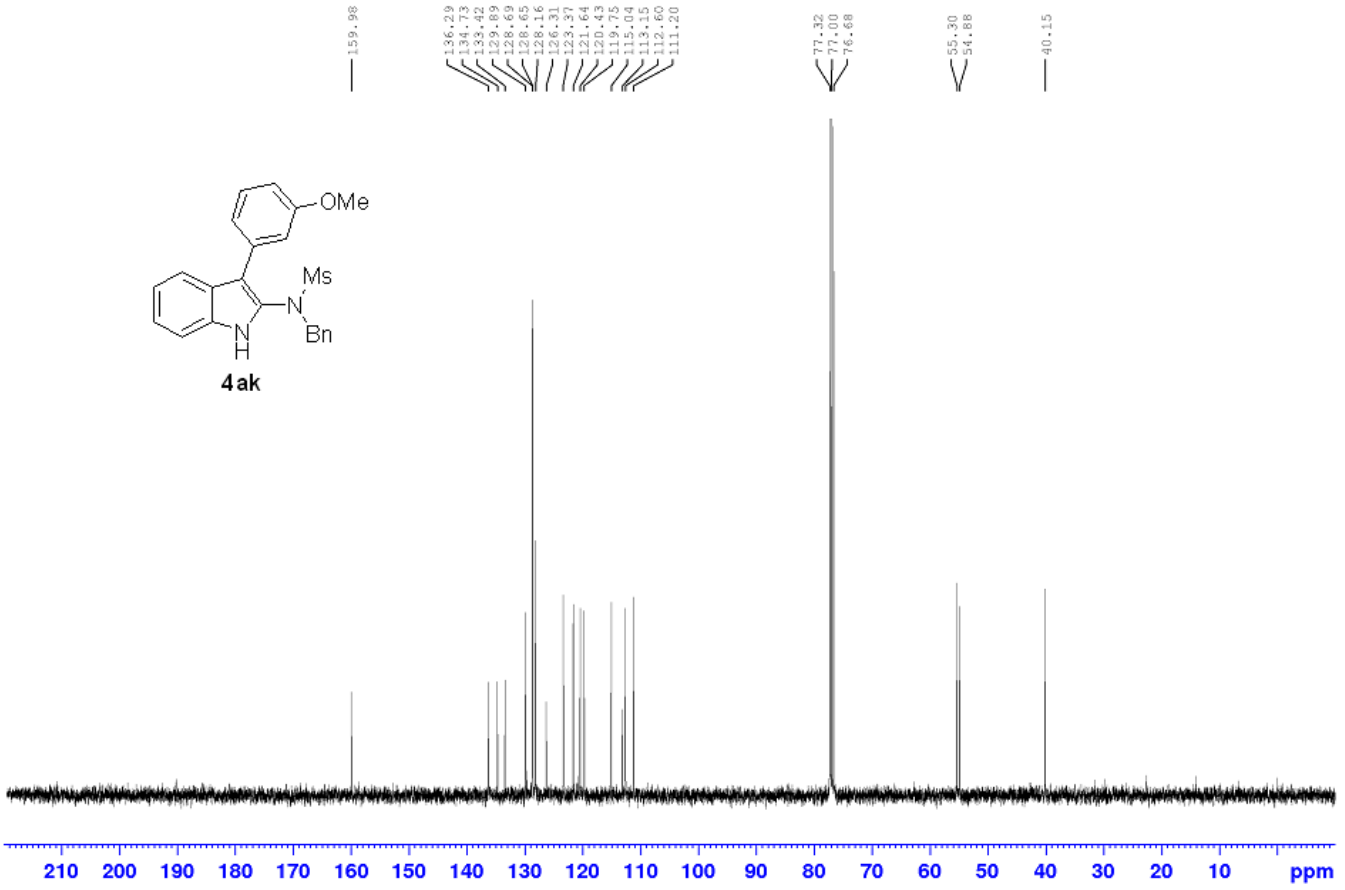
***N*-Benzyl-*N*-(3-(4-nitrophenyl)-1*H*-indol-2-yl)methanesulfonamide (4aj)**



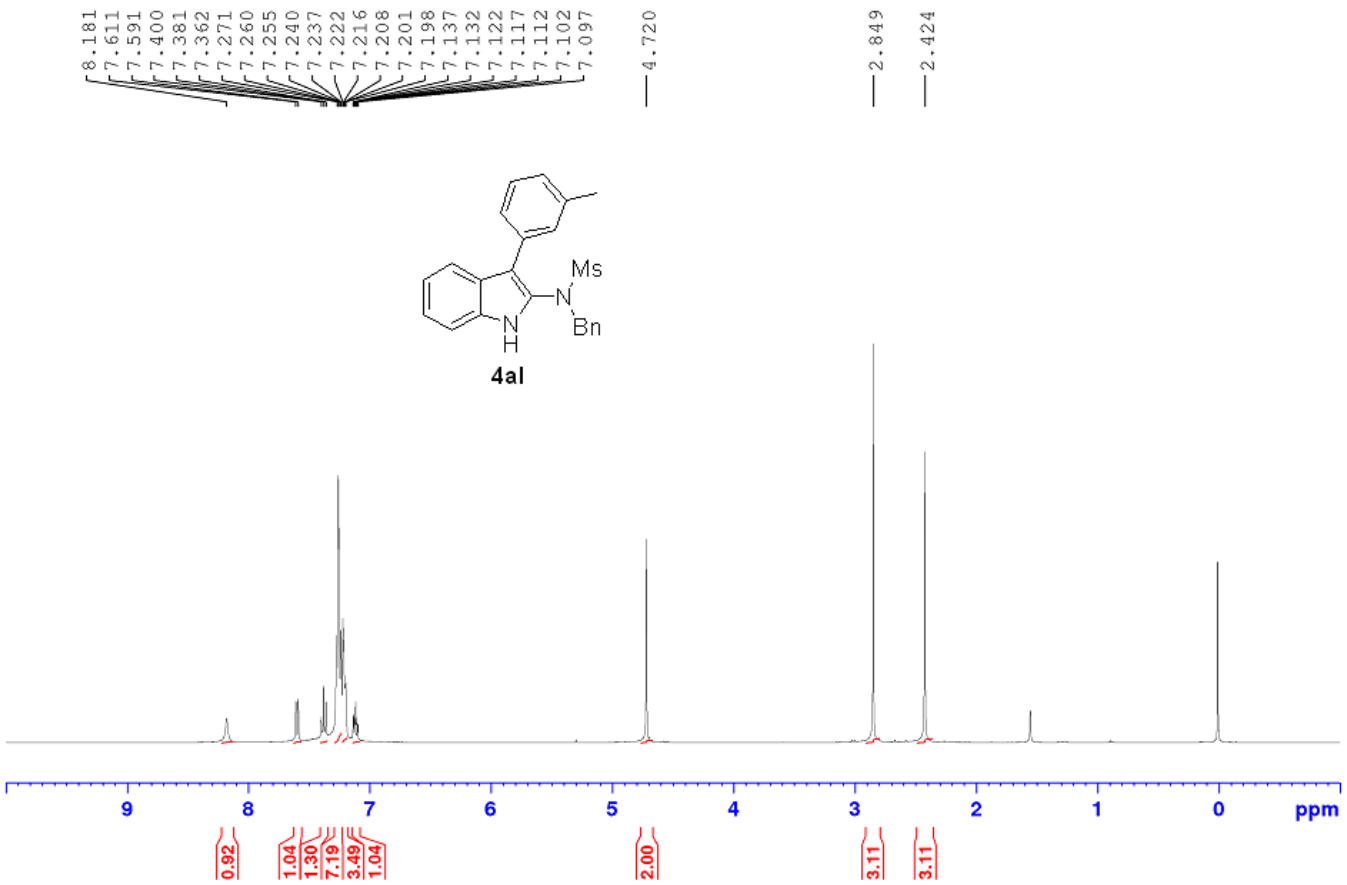


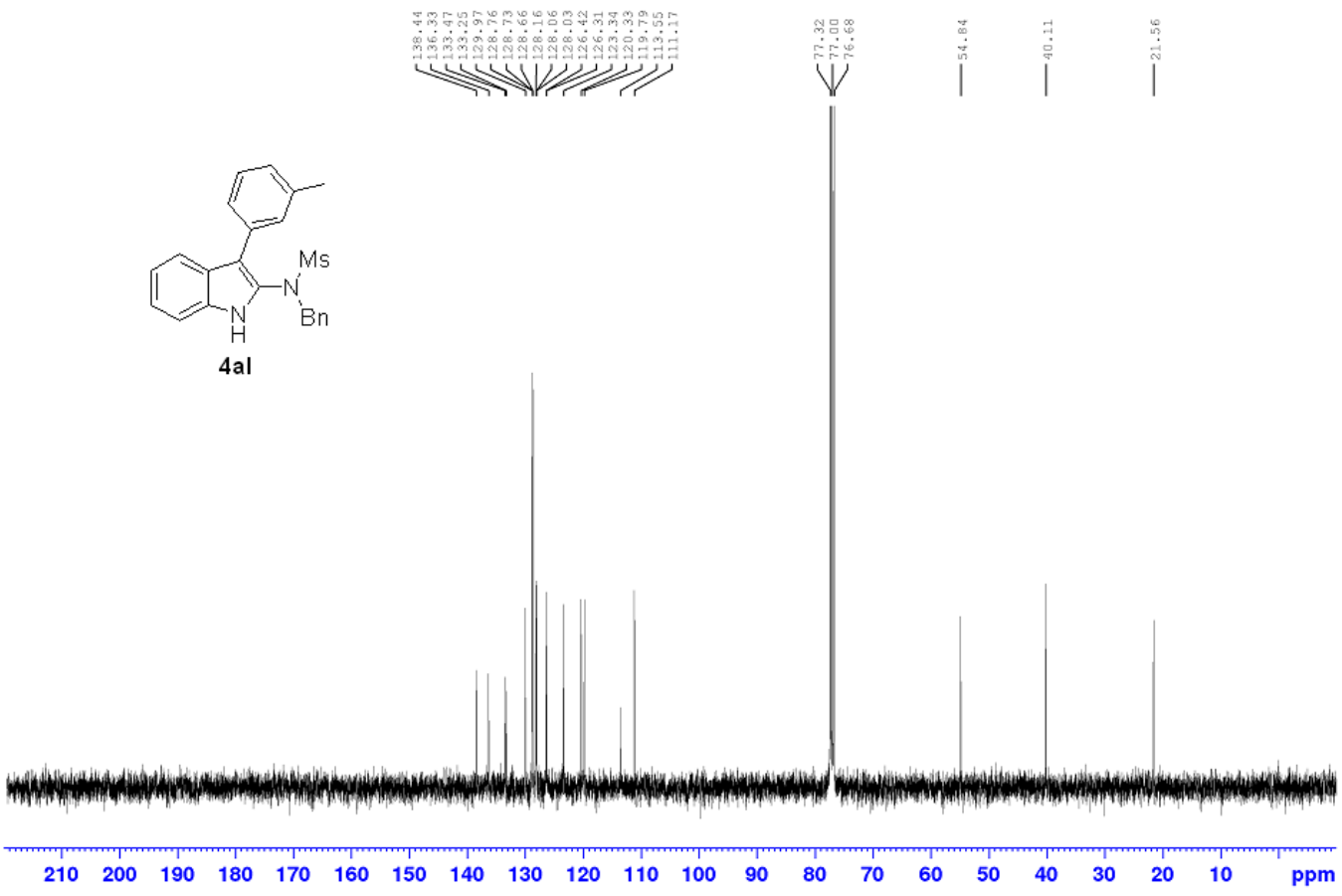
_N_-Benzyl-_N_-(3-(3-methoxyphenyl)-1_H_-indol-2-yl)methanesulfonamide (4ak)



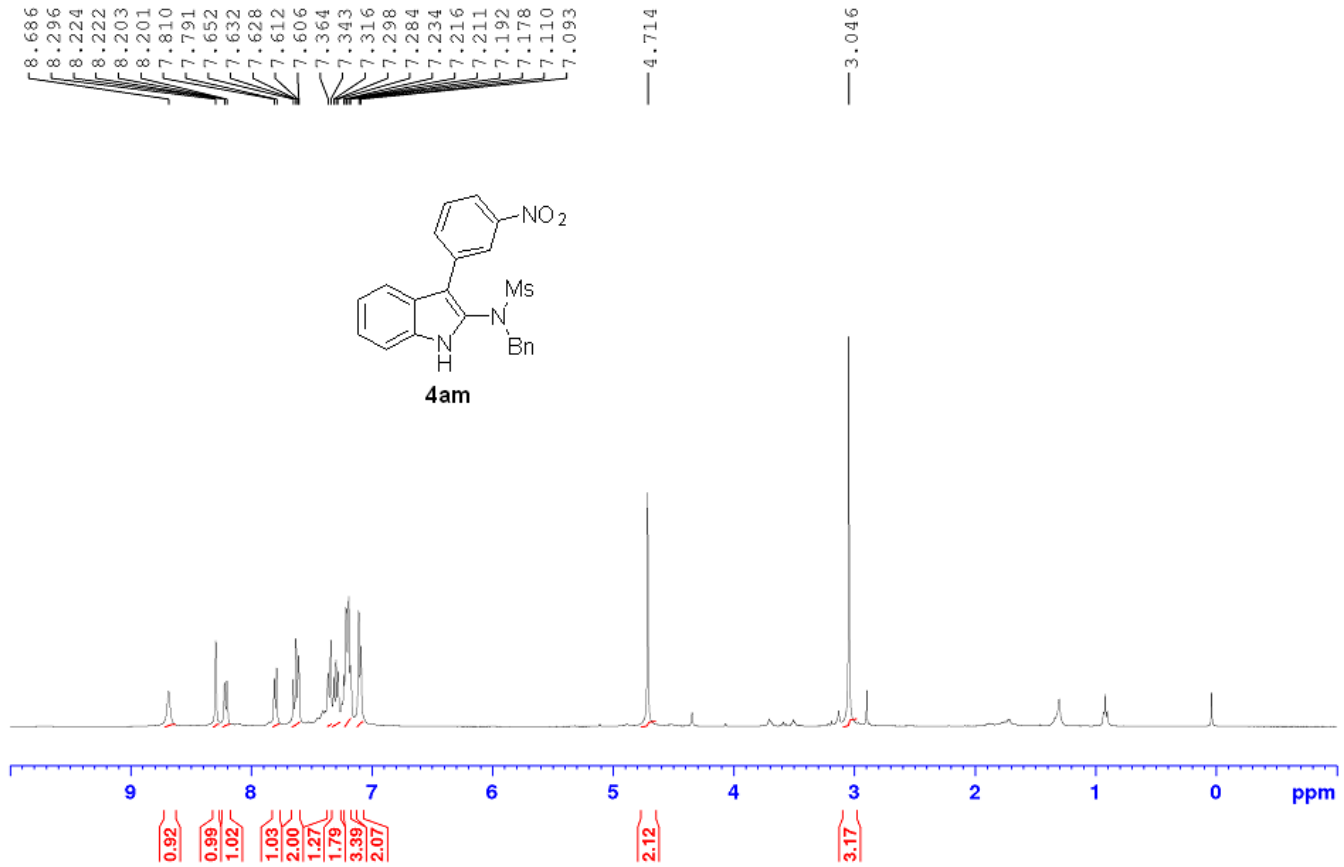


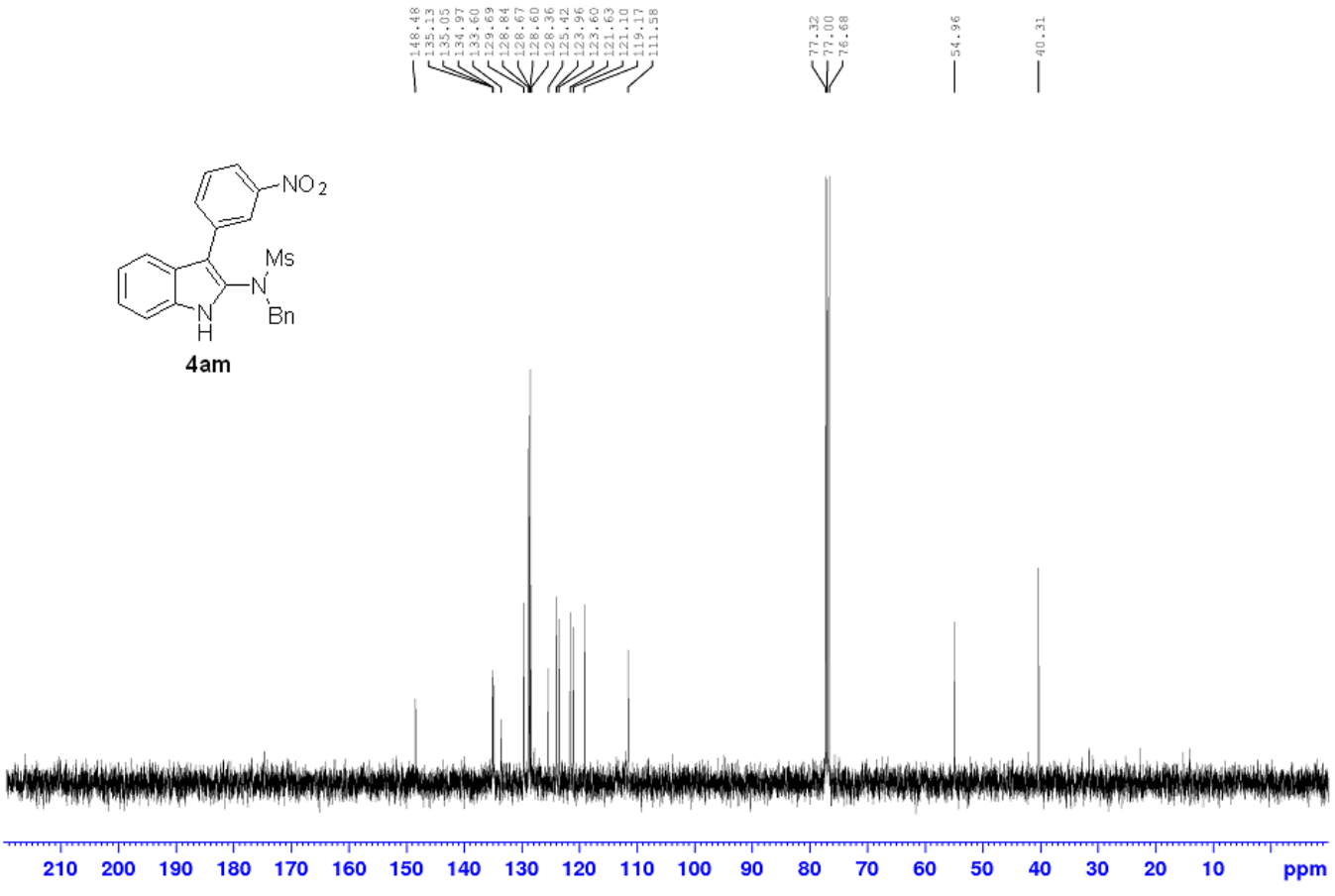
_N_-Benzyl-_N_-(3-(_m_-tolyl)-1_H_-indol-2-yl)methanesulfonamide (4al)



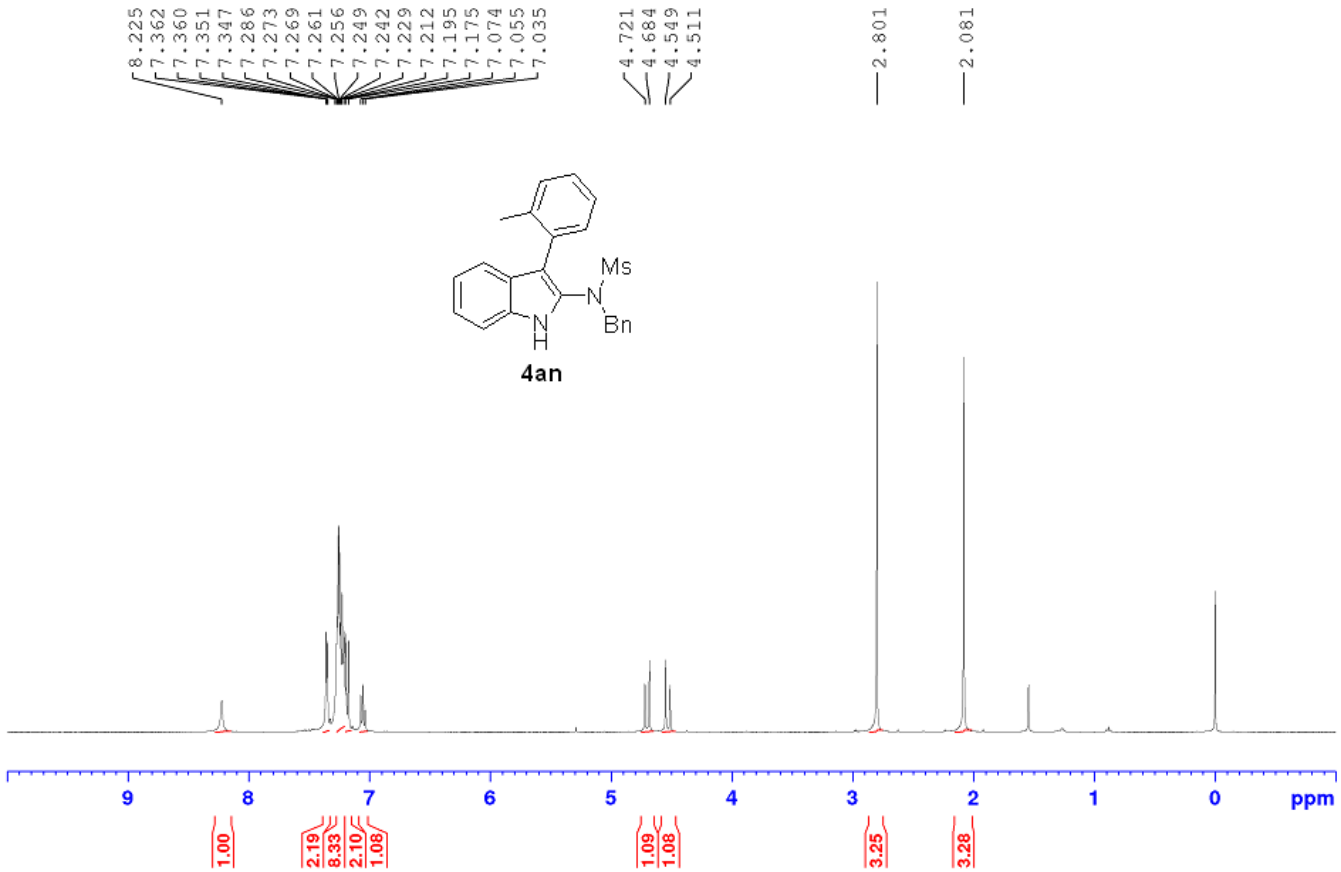


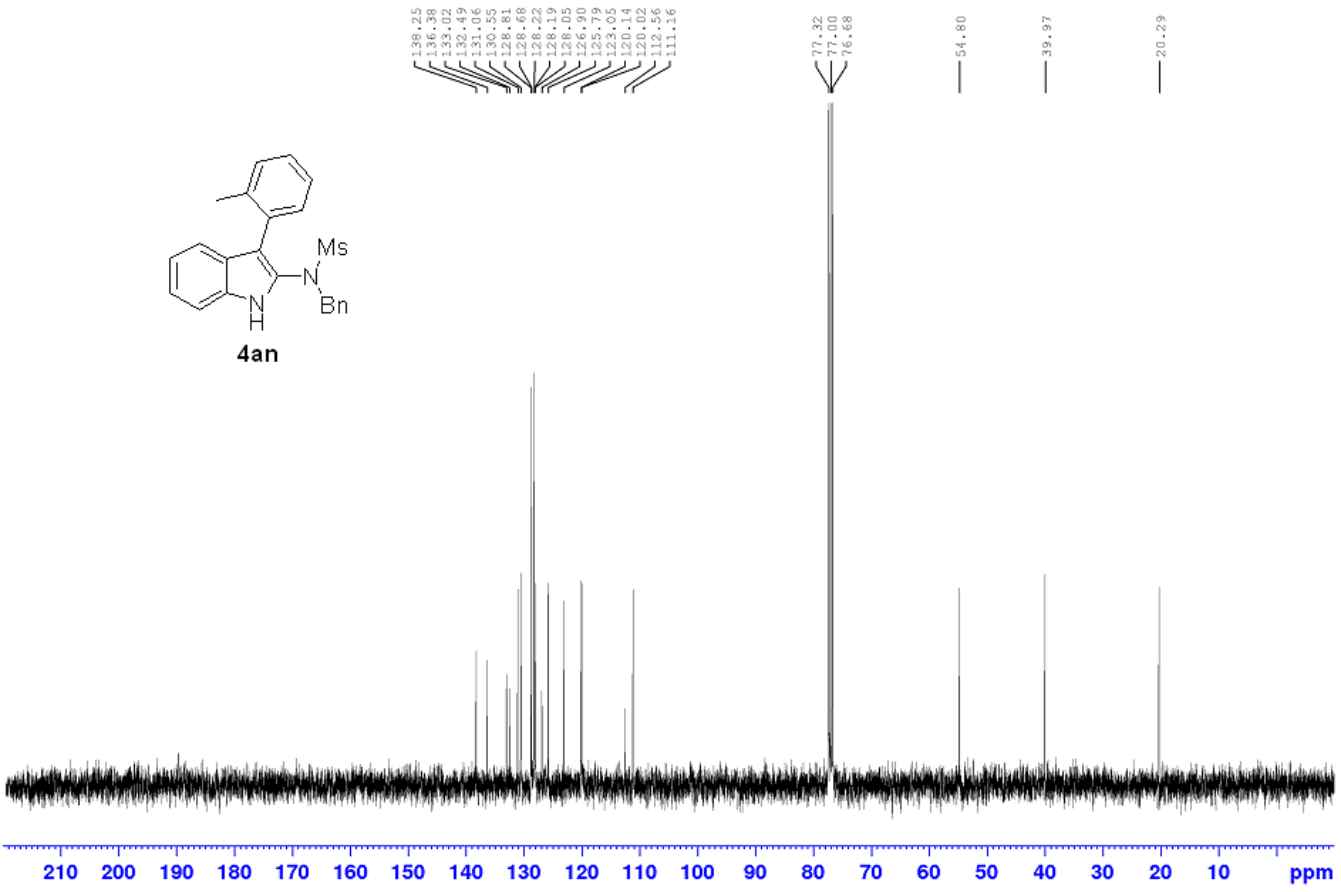
***N*-Benzyl-*N*-(3-(3-nitrophenyl)-1*H*-indol-2-yl)methanesulfonamide (4am)**



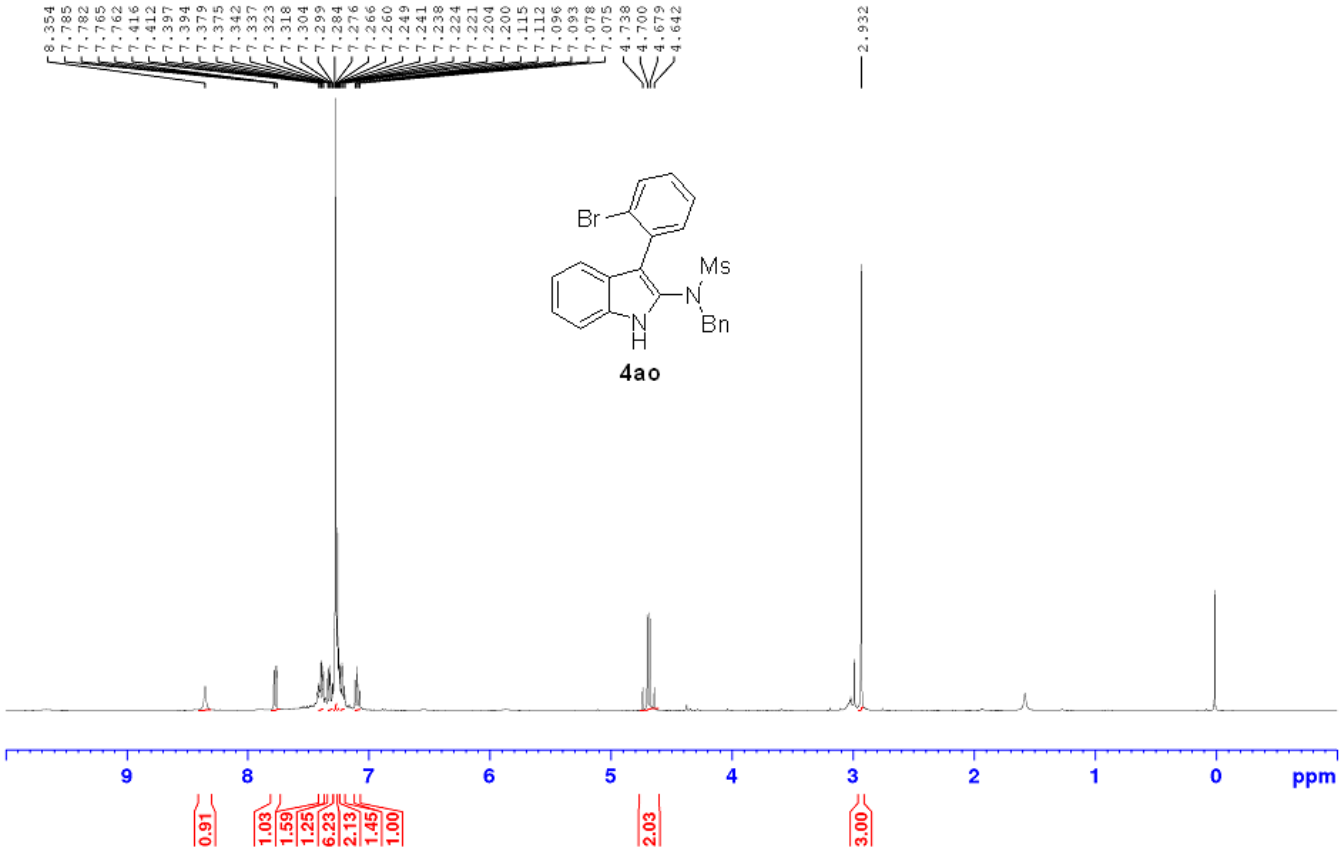


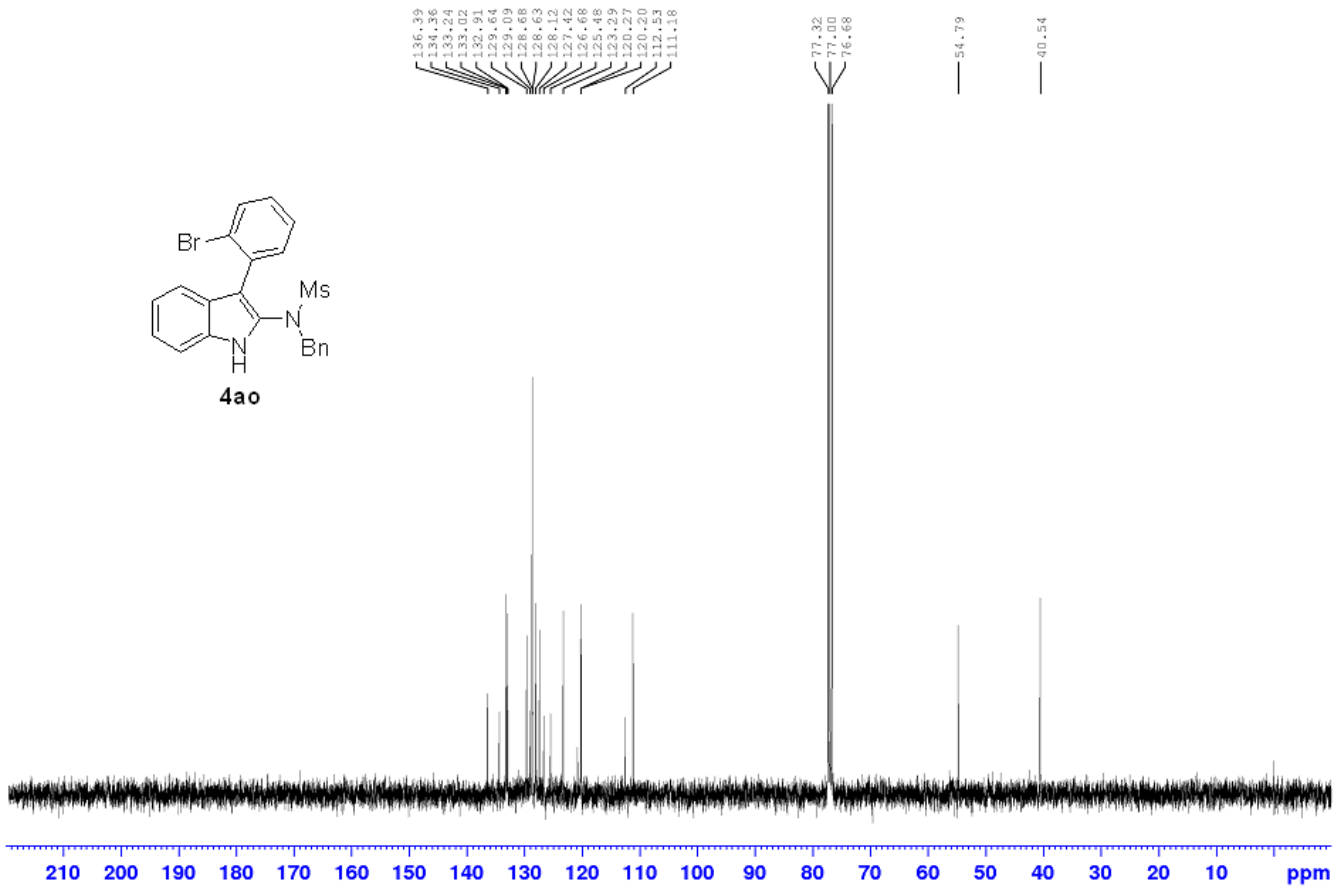
_N_-Benzyl-_N_-(3-(_o_-tolyl)-1_H_-indol-2-yl)methanesulfonamide (4an)



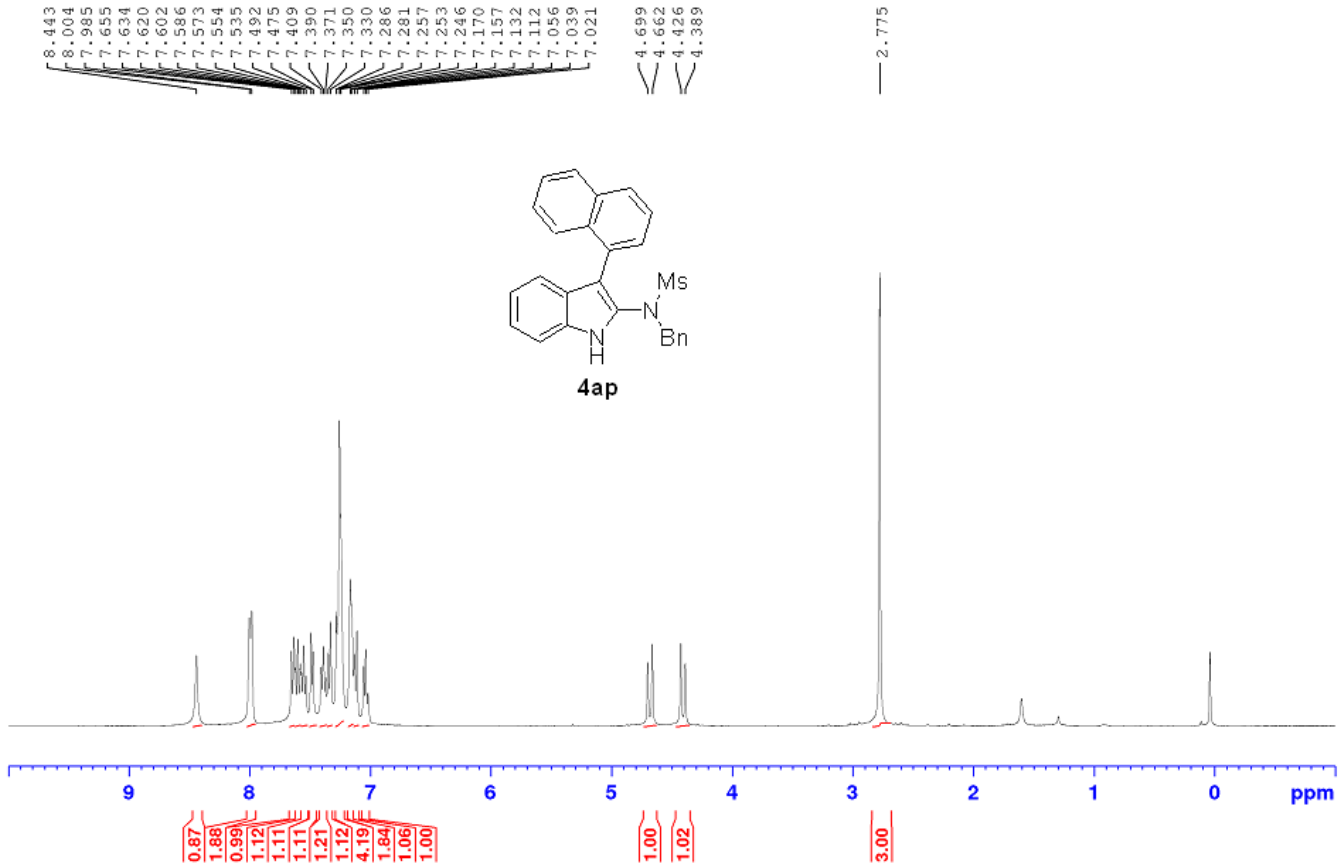


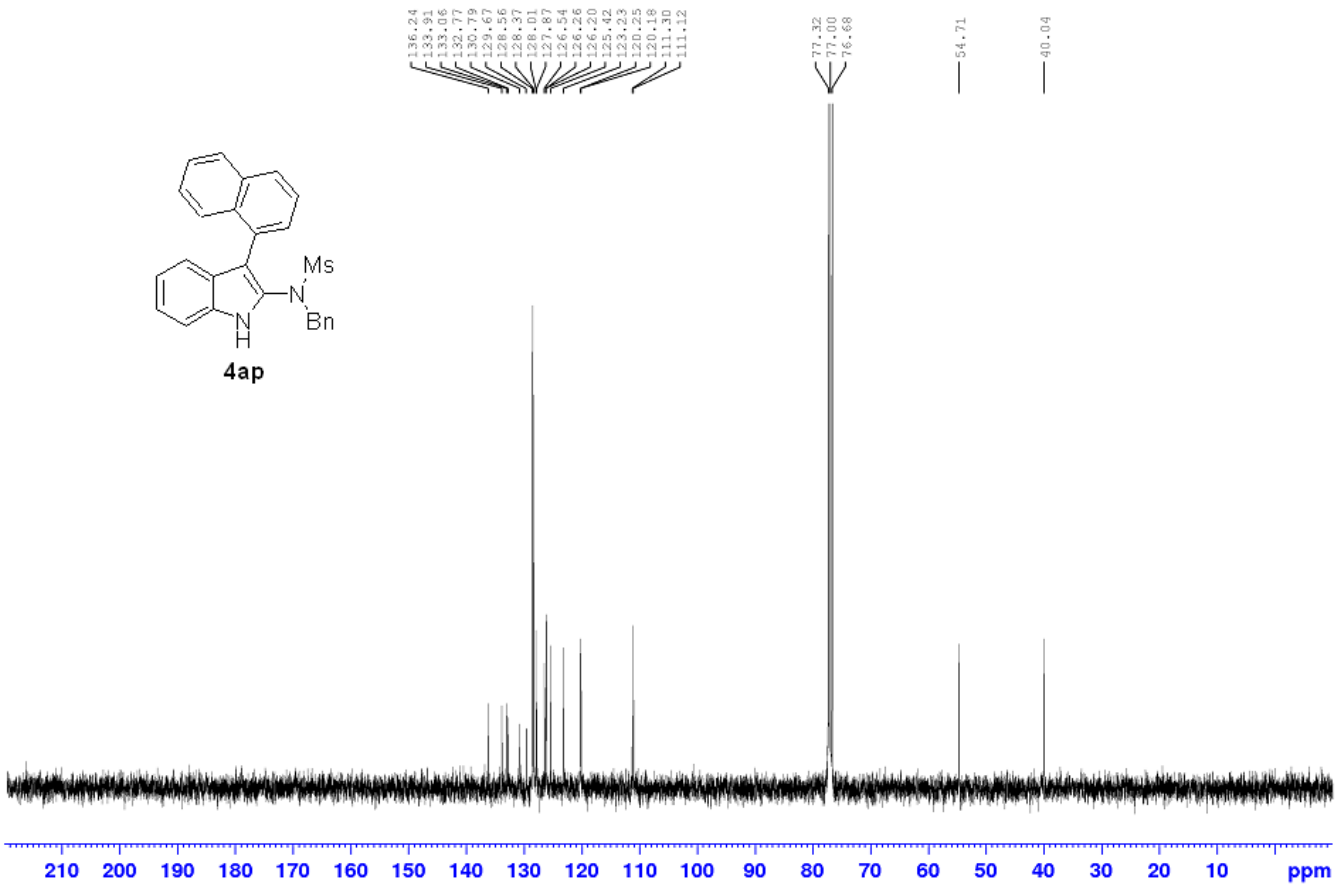
_N_-Benzyl-_N_-(3-(2-bromophenyl)-1_H_-indol-2-yl)methanesulfonamide (4ao)



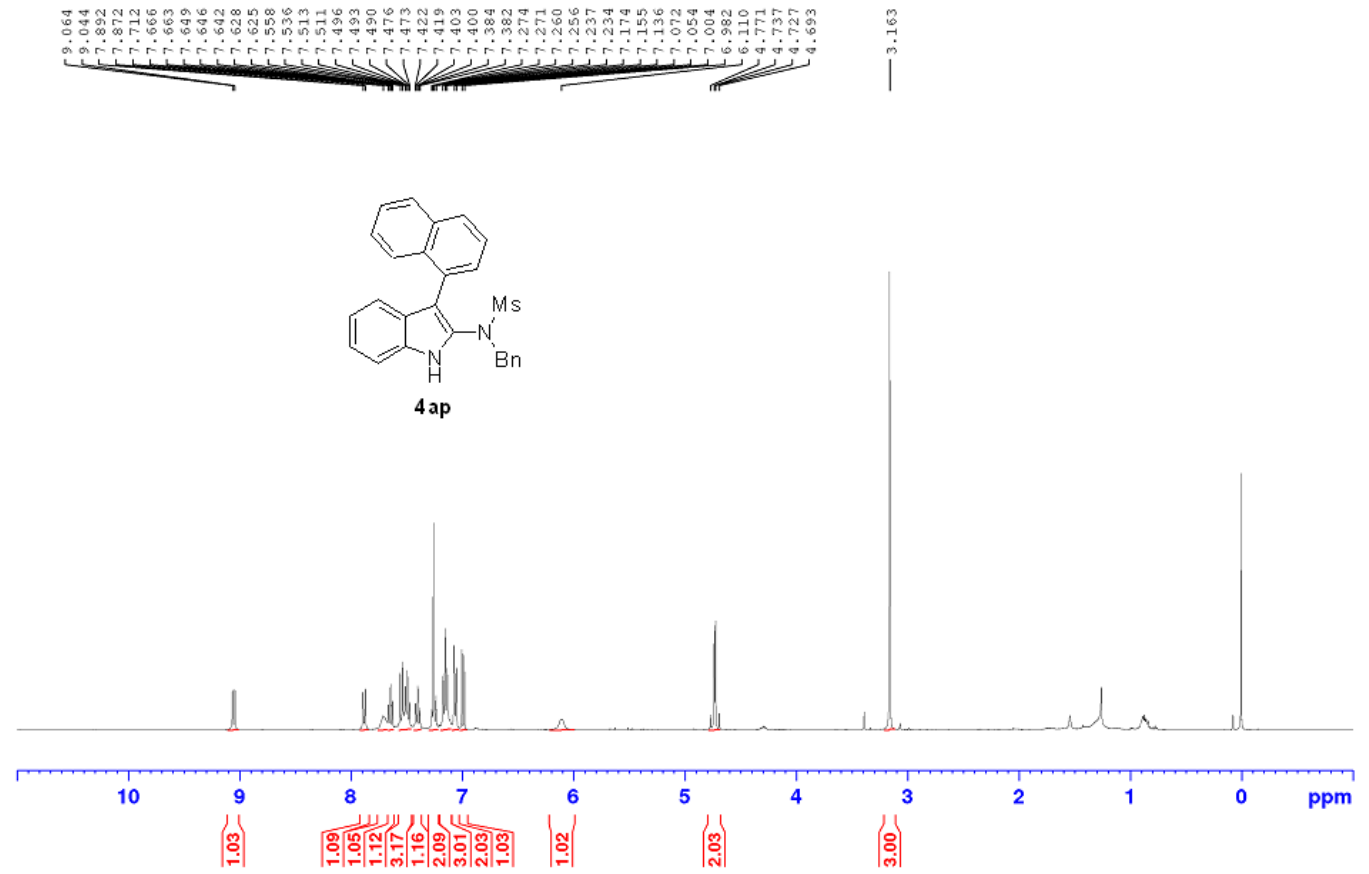


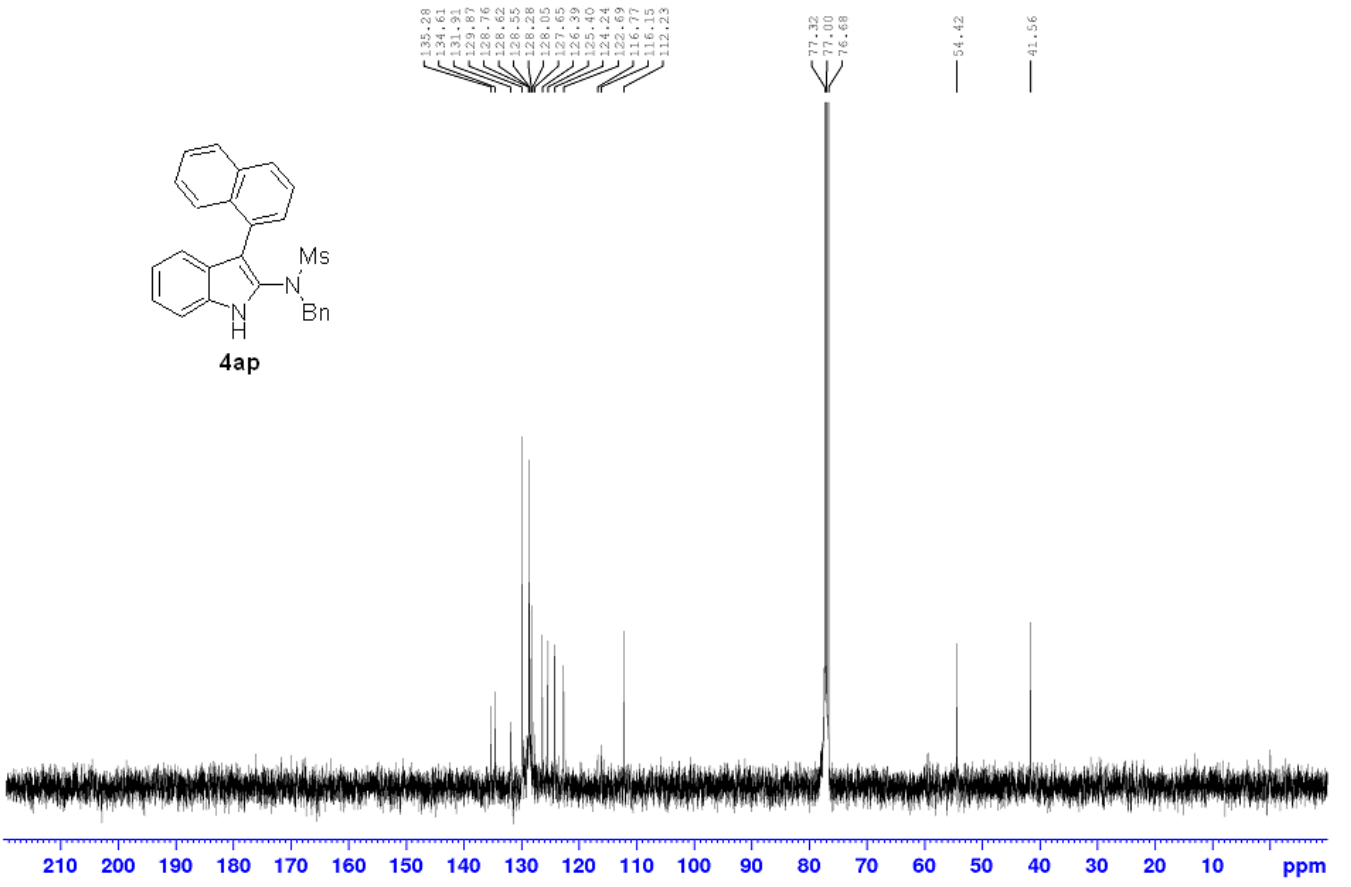
_N_-Benzyl-_N_-(3-(naphthalen-1-yl)-1_H_-indol-2-yl)methanesulfonamide (4ap) - A



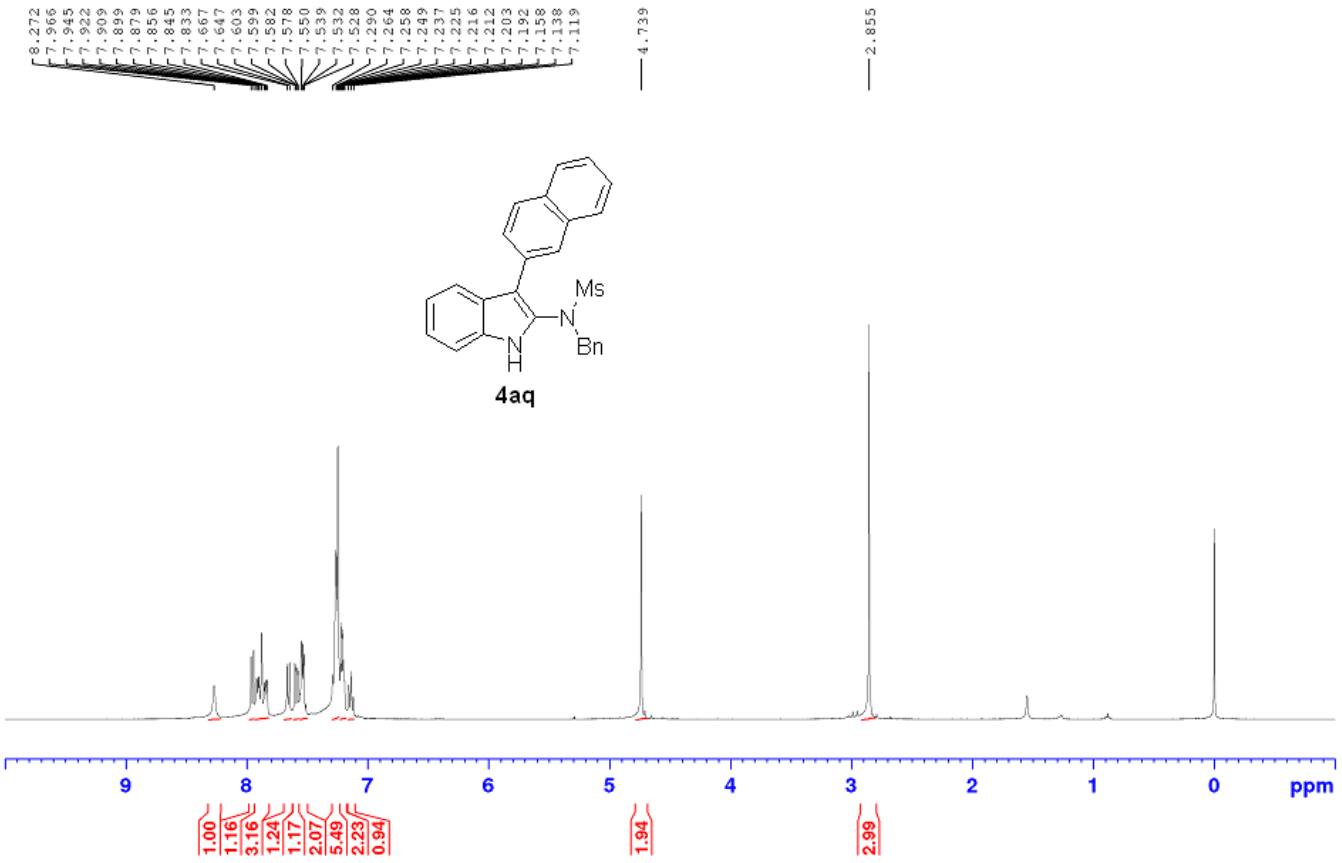


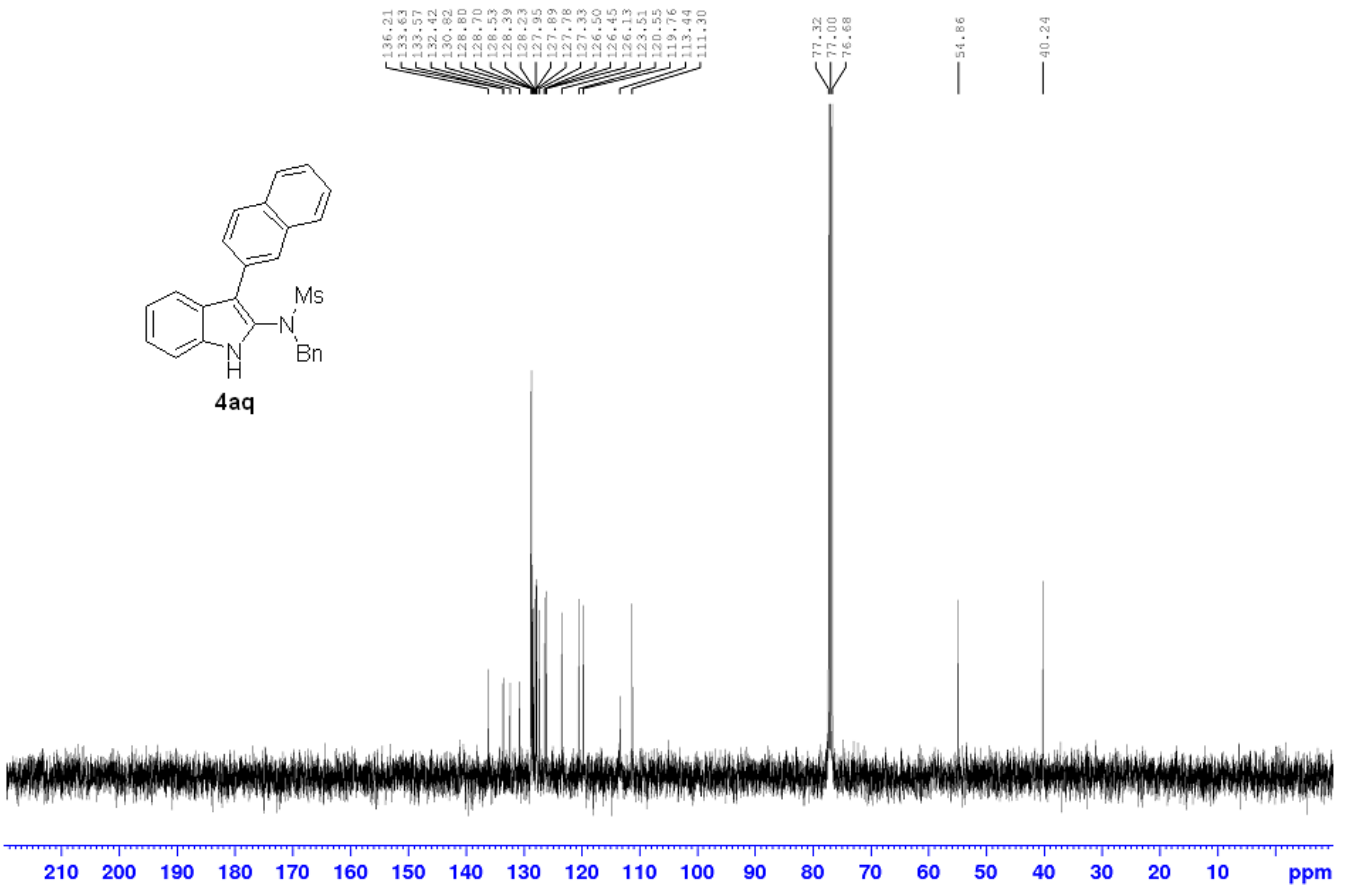
_N_-Benzyl-_N_-(3-(naphthalen-1-yl)-1_H_-indol-2-yl)methanesulfonamide (4ap) - B



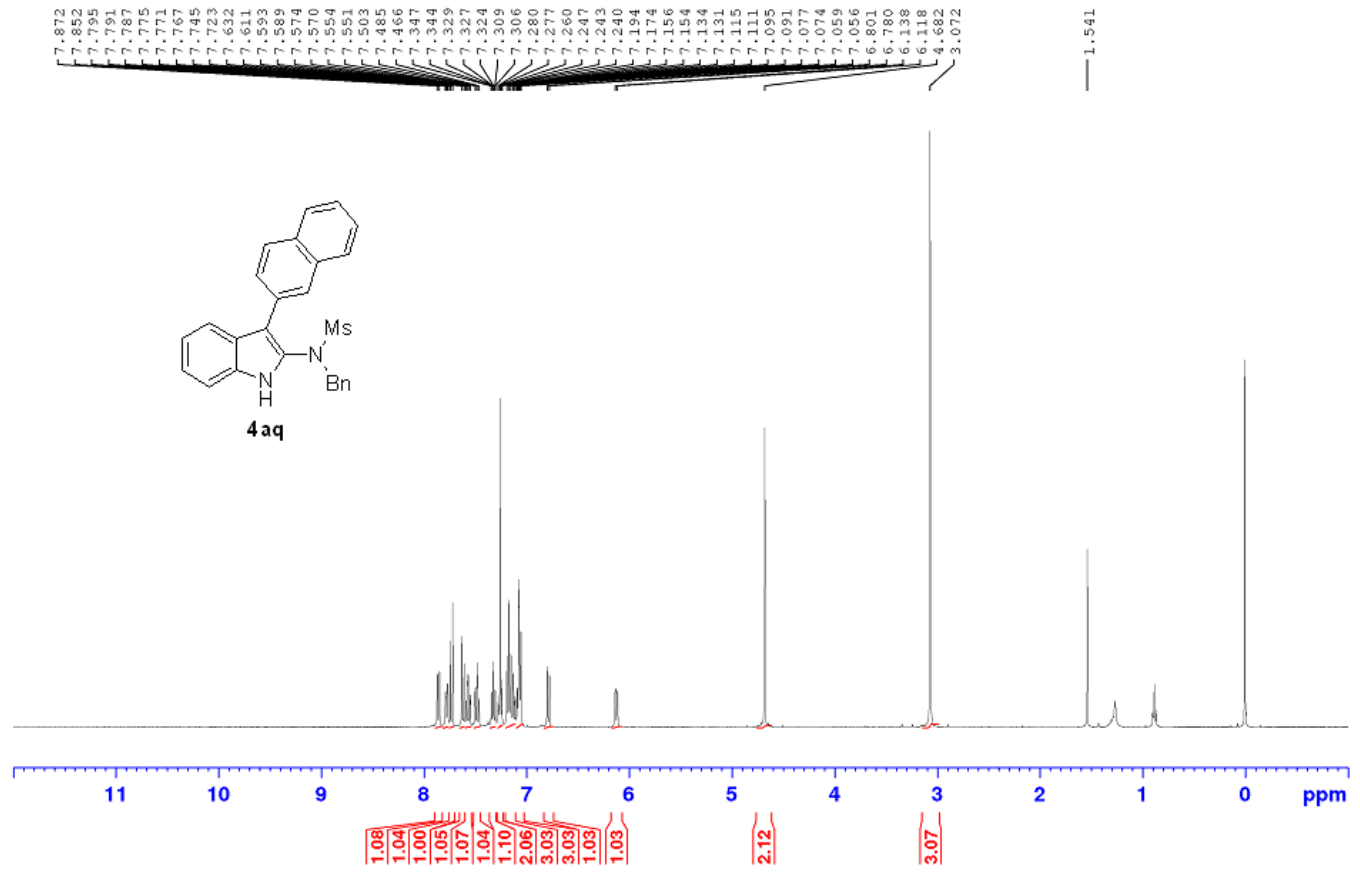


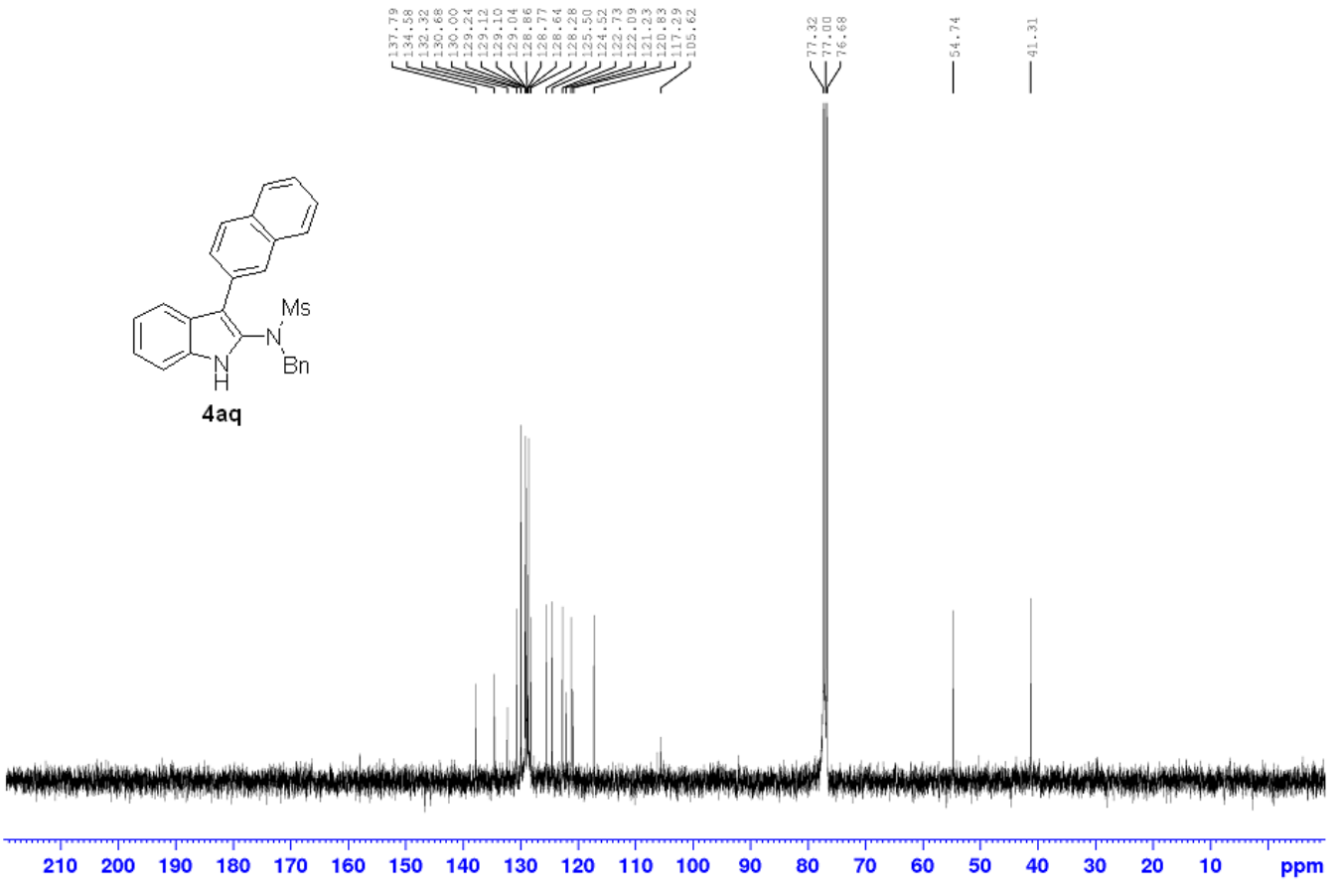
_N_-Benzyl-_N_-(3-(naphthalen-2-yl)-1_H_-indol-2-yl)methanesulfonamide (4aq) - A



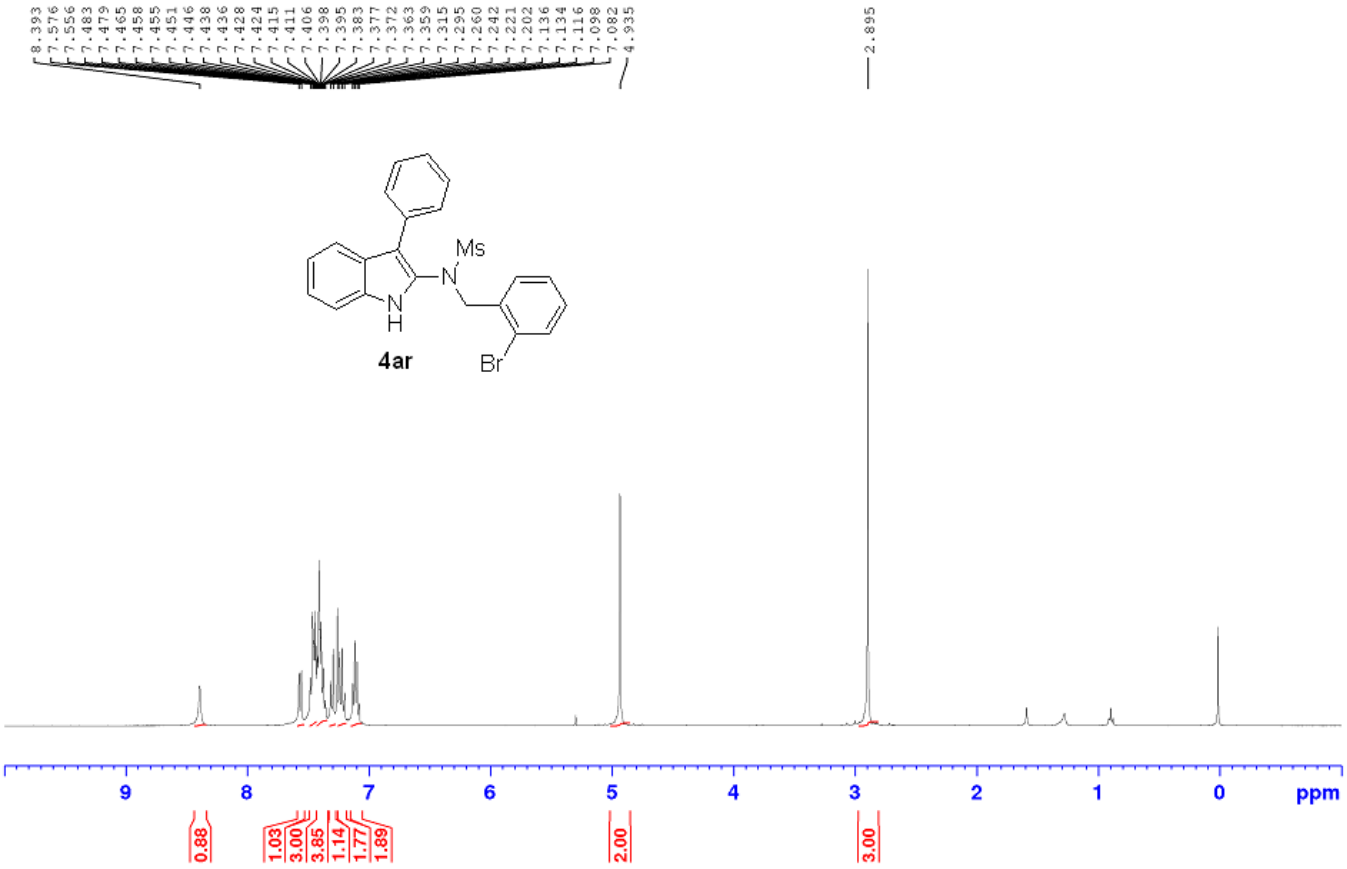


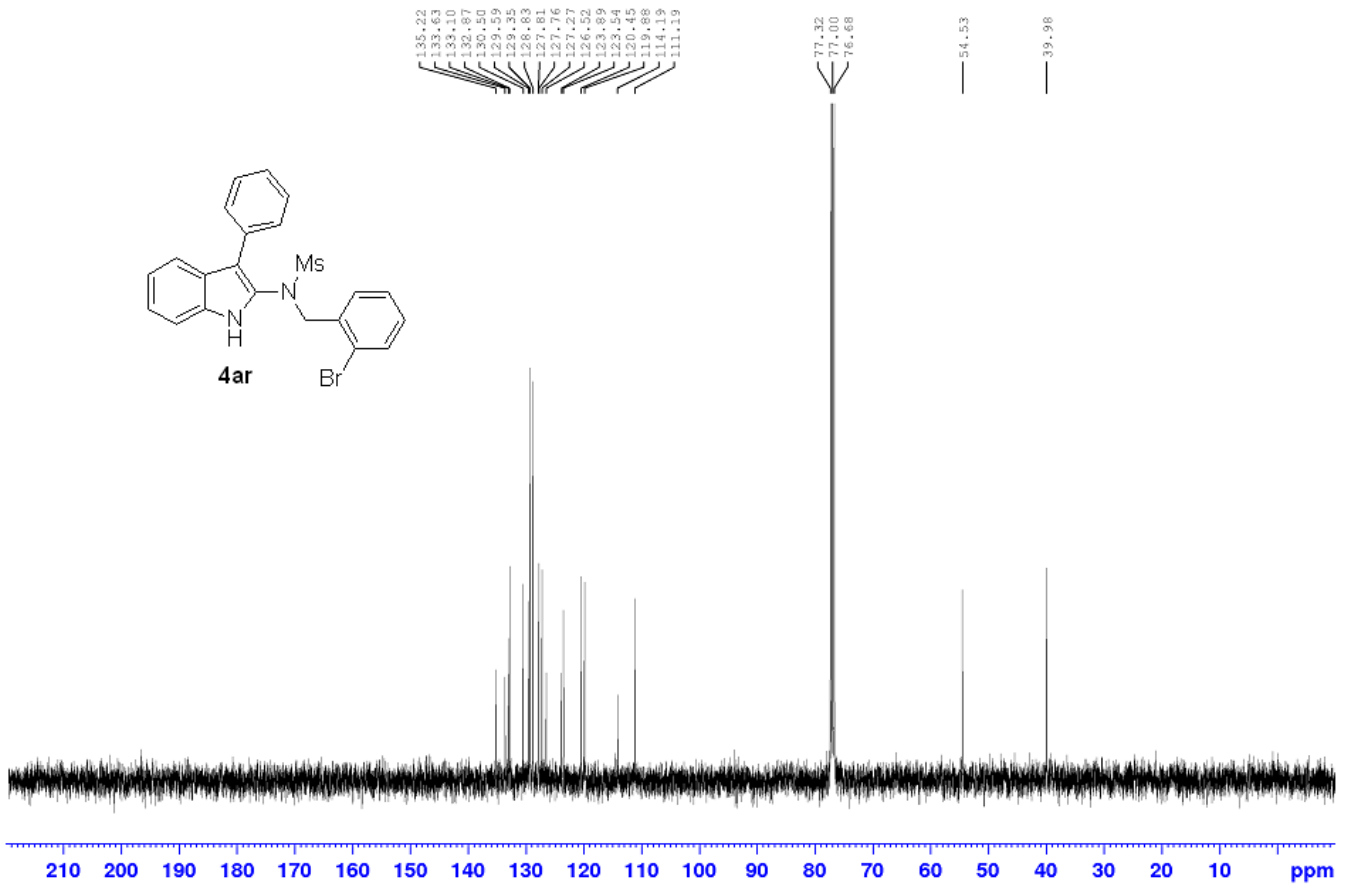
_N_-Benzyl-_N_-(3-(naphthalen-2-yl)-1_H_-indol-2-yl)methanesulfonamide (4aq) - B



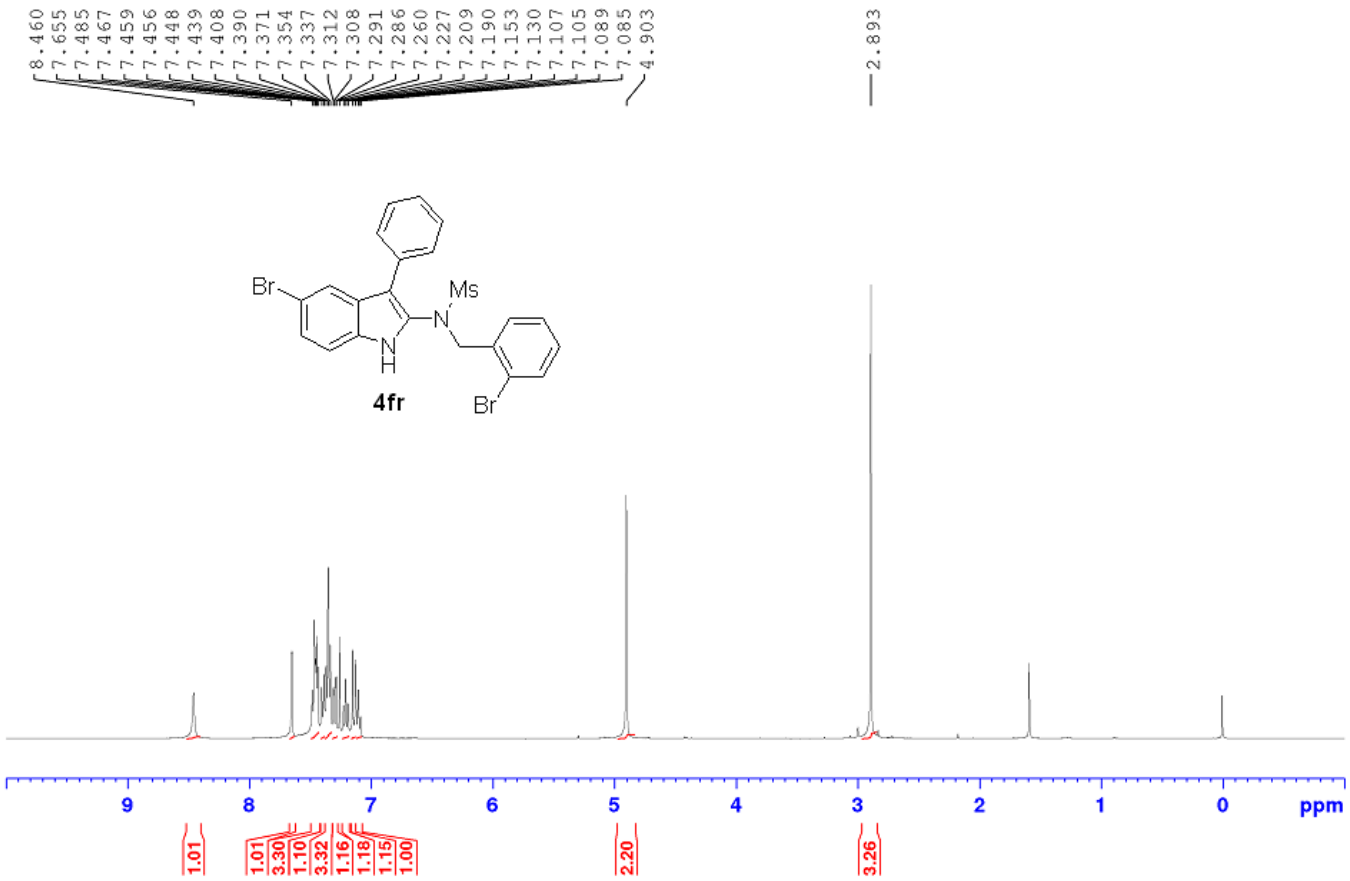


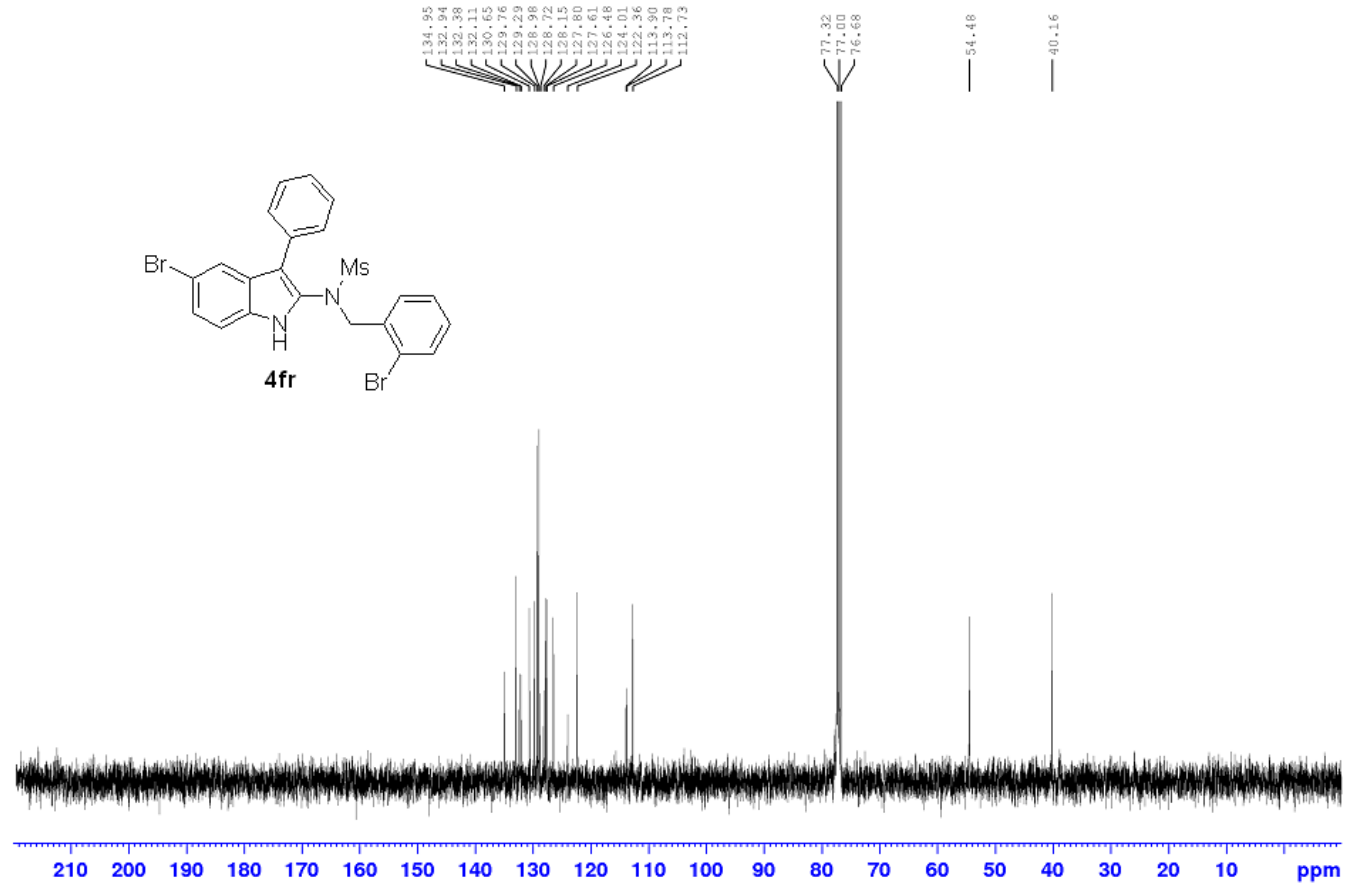
_N_-(2-Bromobenzyl)-_N_-(3-phenyl-1_H_-indol-2-yl)methanesulfonamide (4ar)



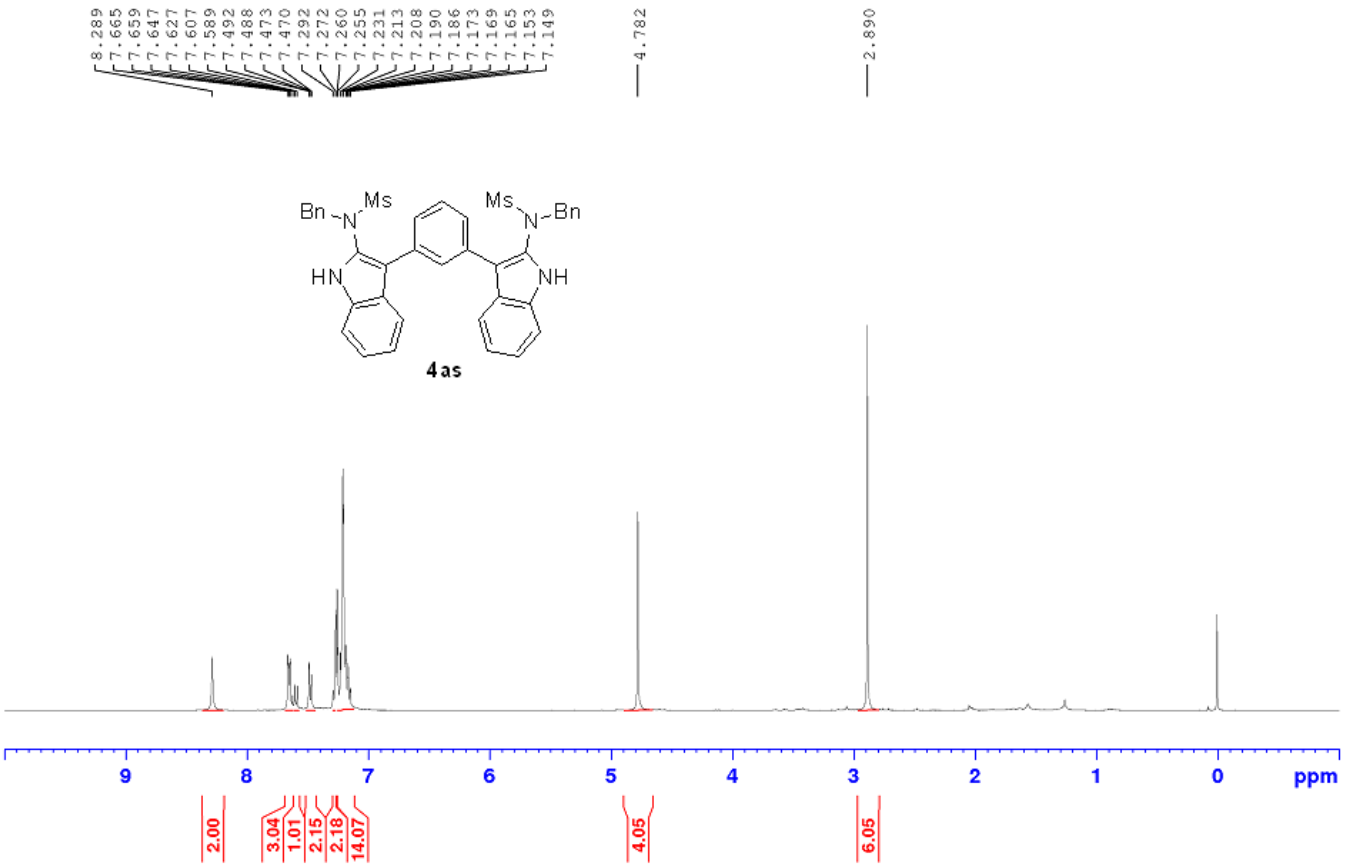


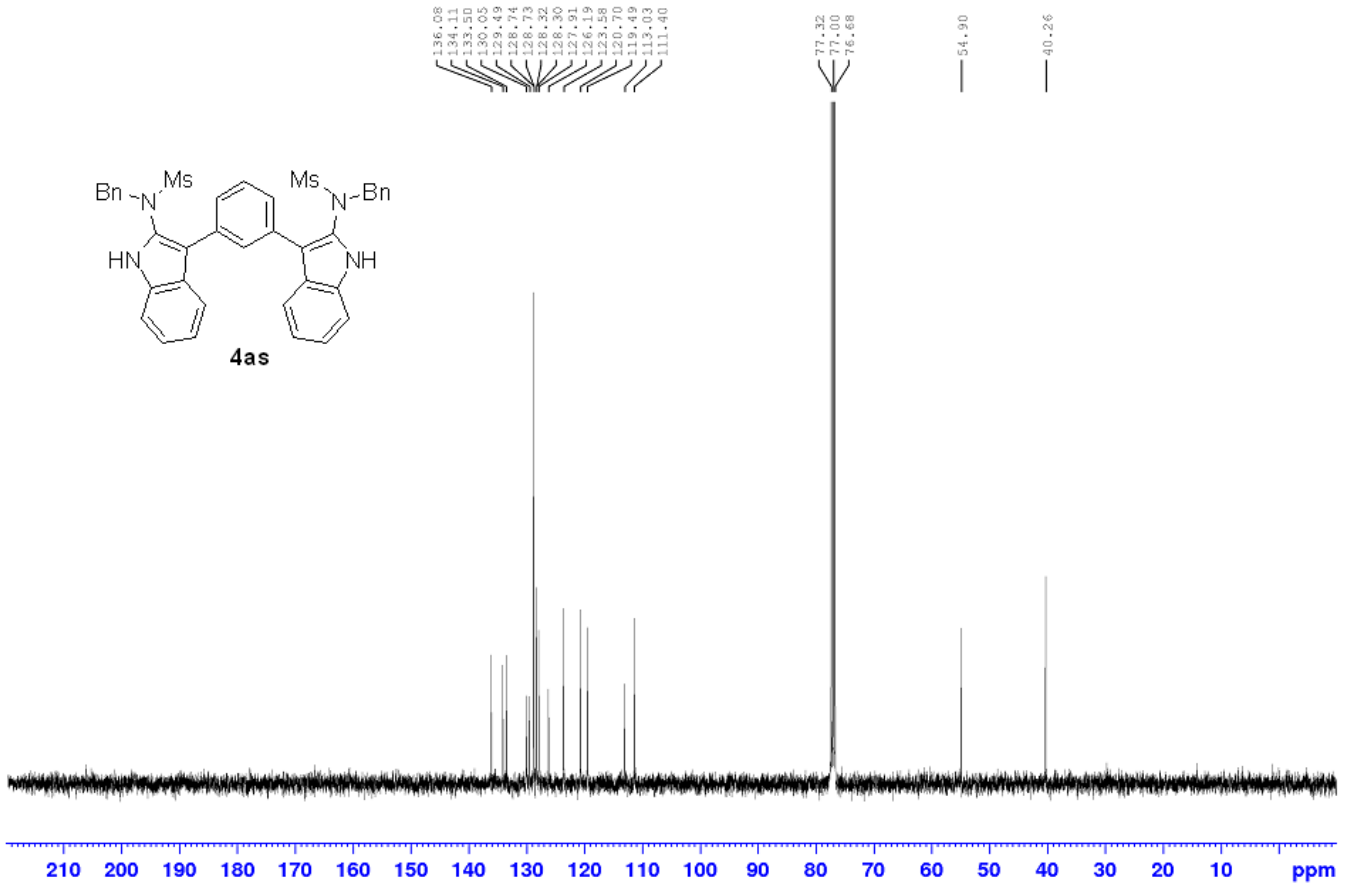
***N*-(5-Bromo-3-phenyl-1*H*-indol-2-yl)-*N*-(2-bromobenzyl)methanesulfonamide (4fr)**



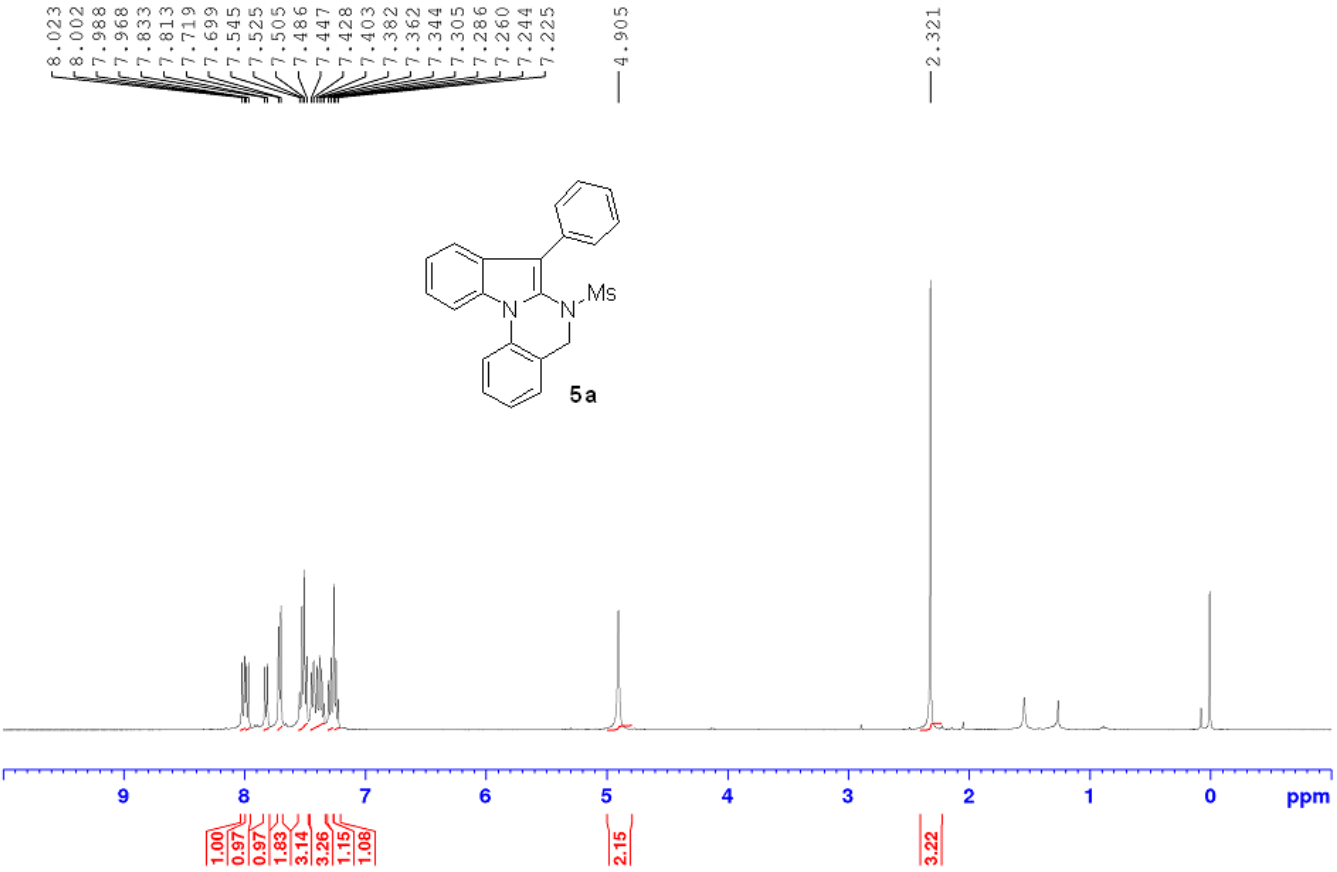


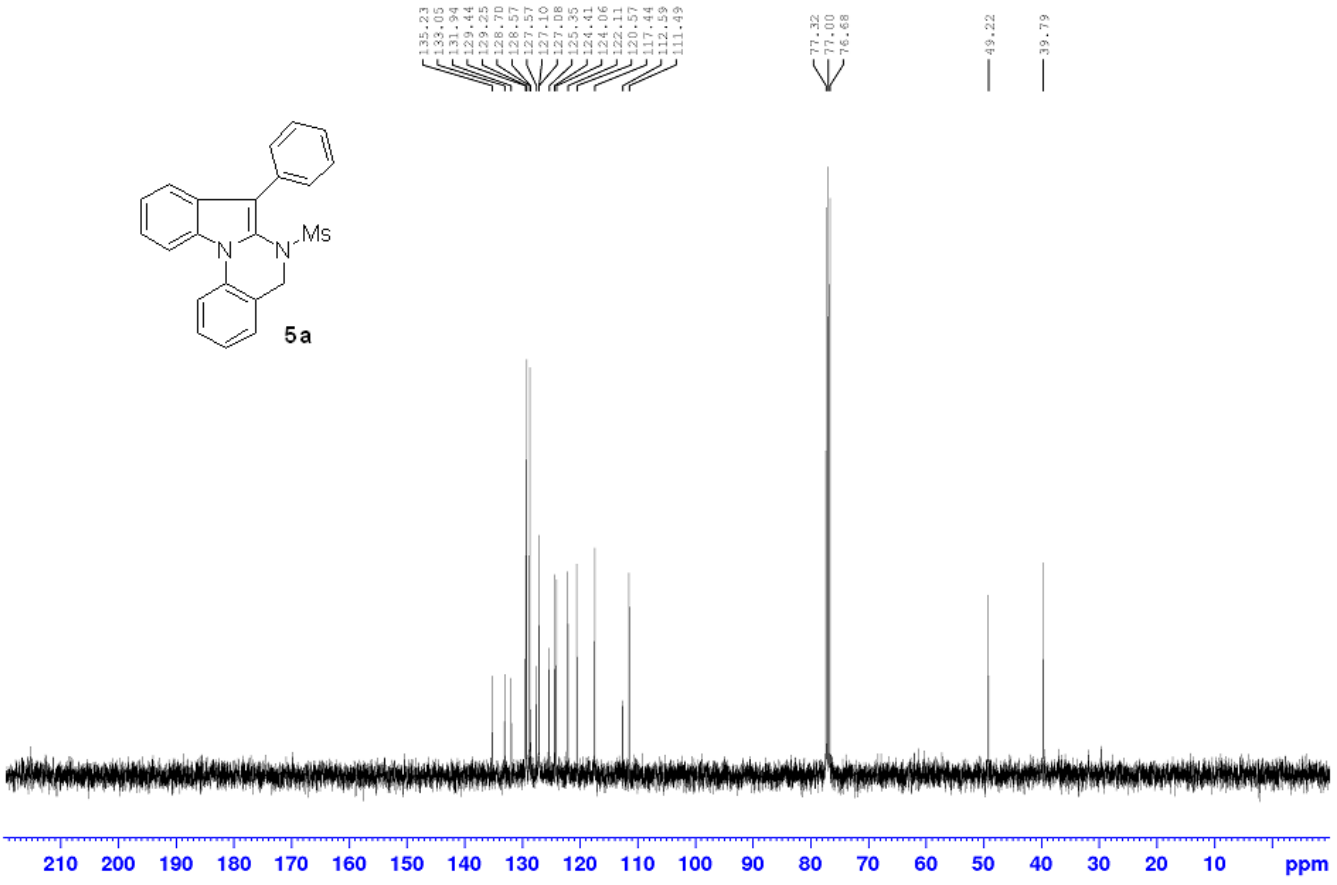
***N,N'*-(1,3-Phenylenebis(1*H*-indole-3,2-diyl))bis(*N*-benzylmethanesulfonamide) (4as)**



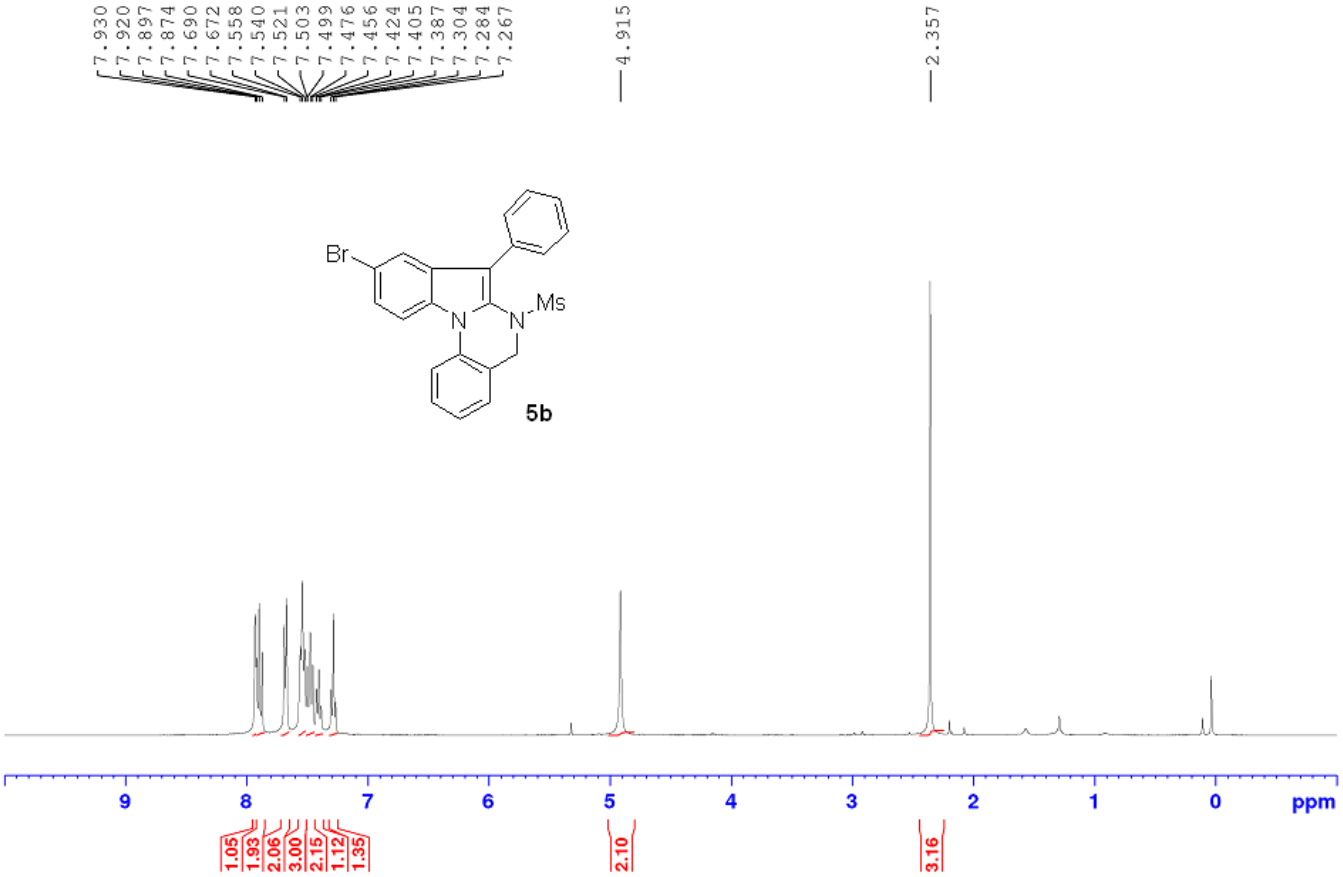


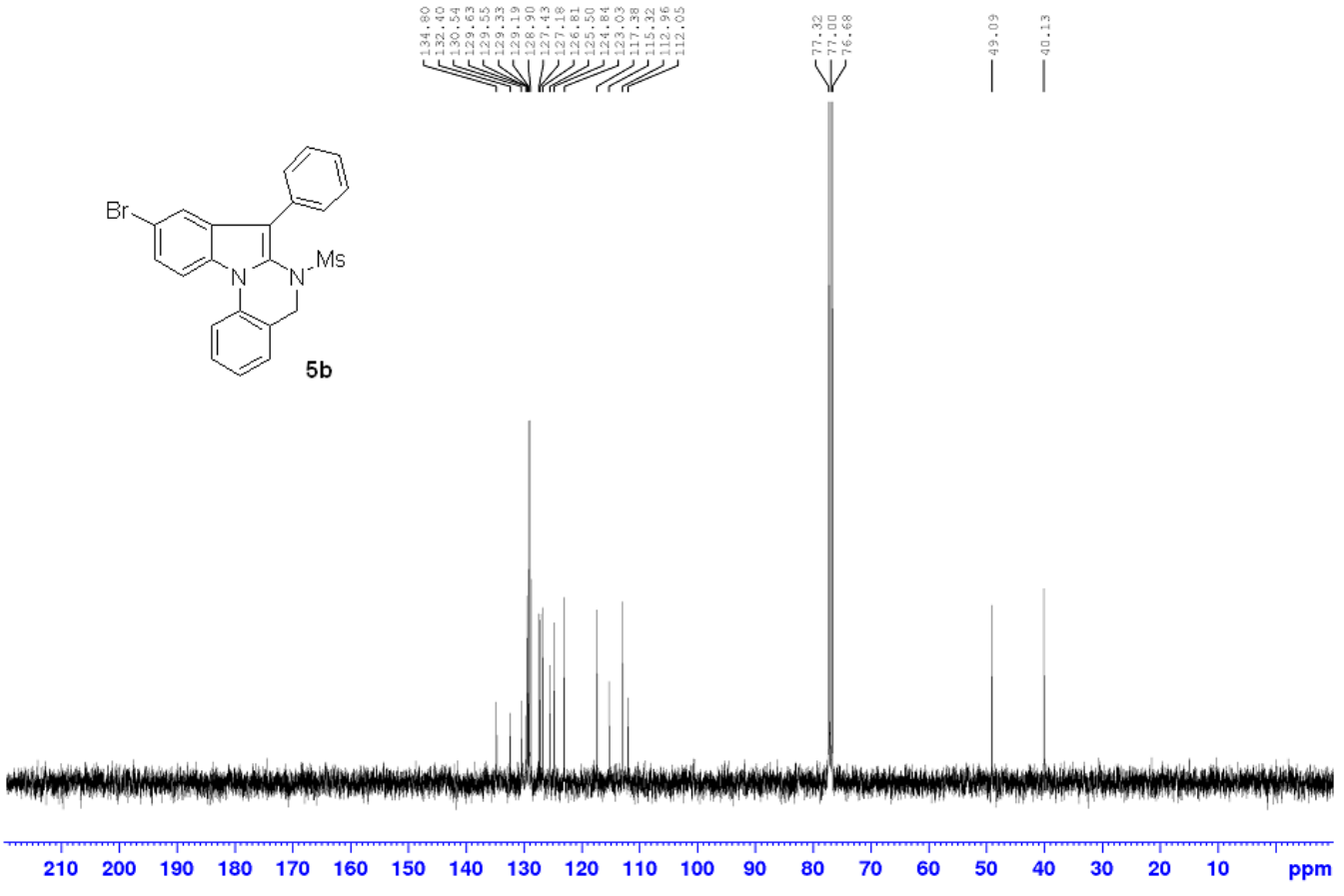
6-(Methylsulfonyl)-7-phenyl-5,6-dihydroindolo[1,2-*a*]quinazoline (5a)



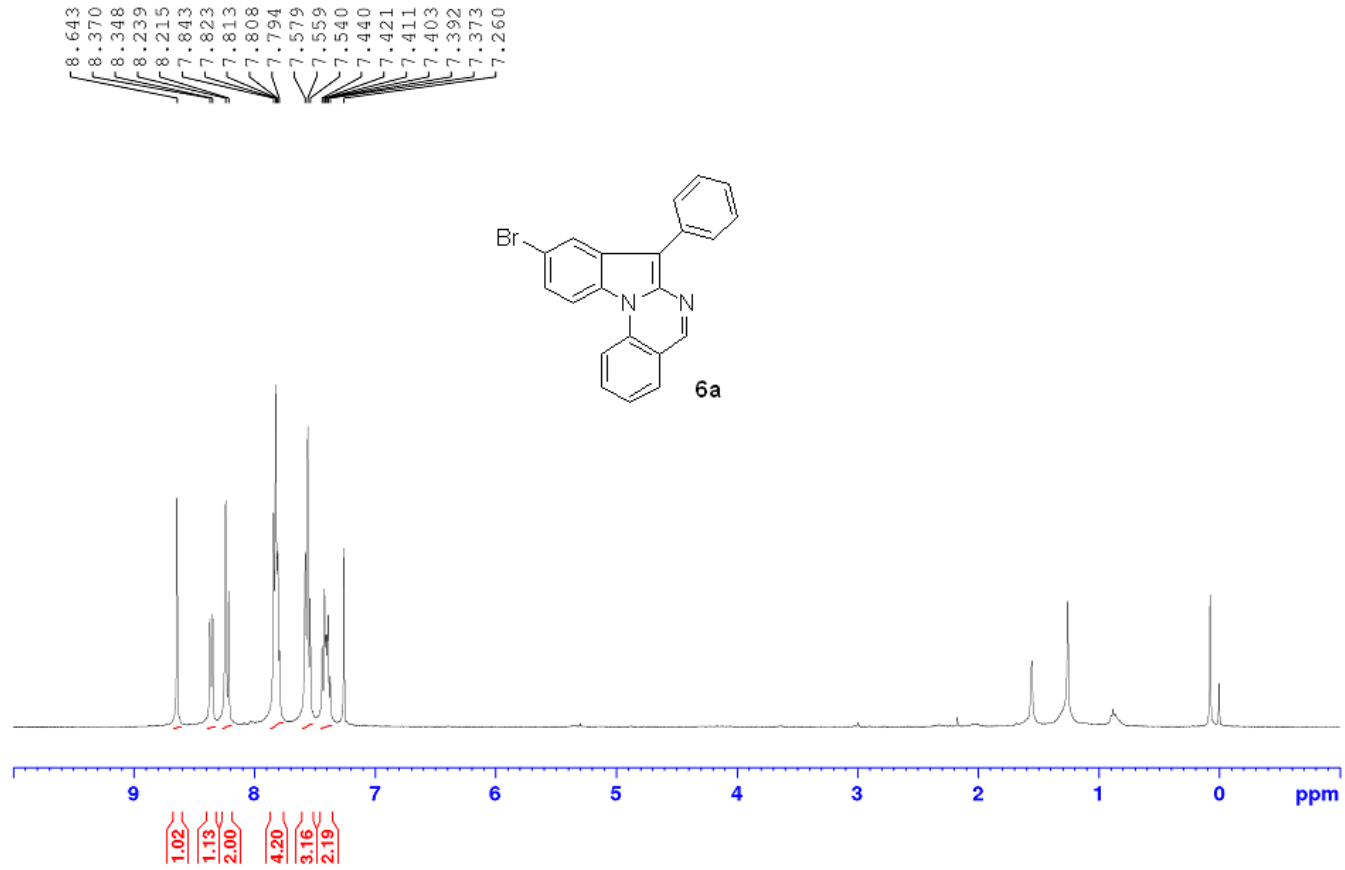


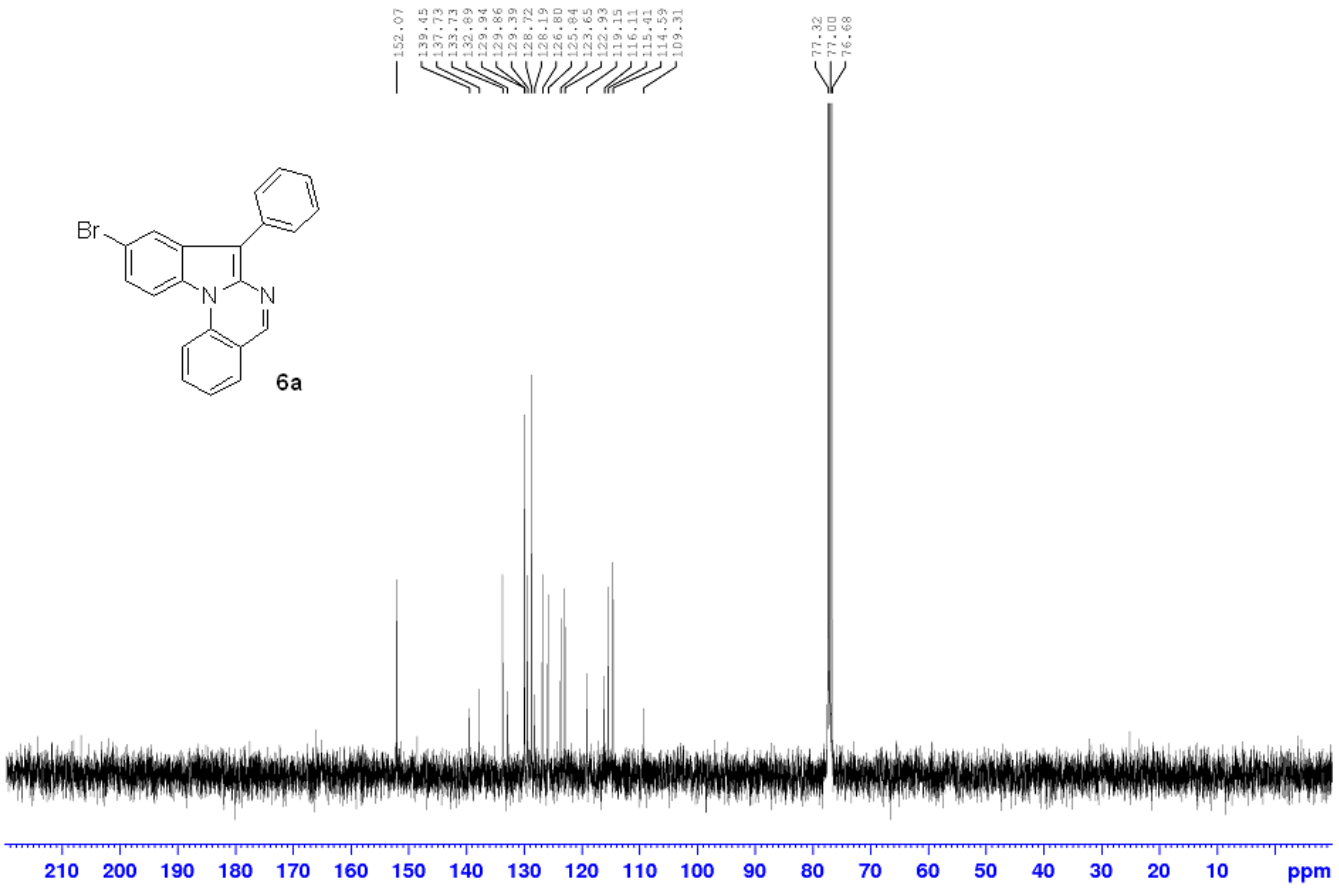
9-Bromo-6-(methylsulfonyl)-7-phenyl-5,6-dihydroindolo[1,2-*a*]quinazoline (5b)



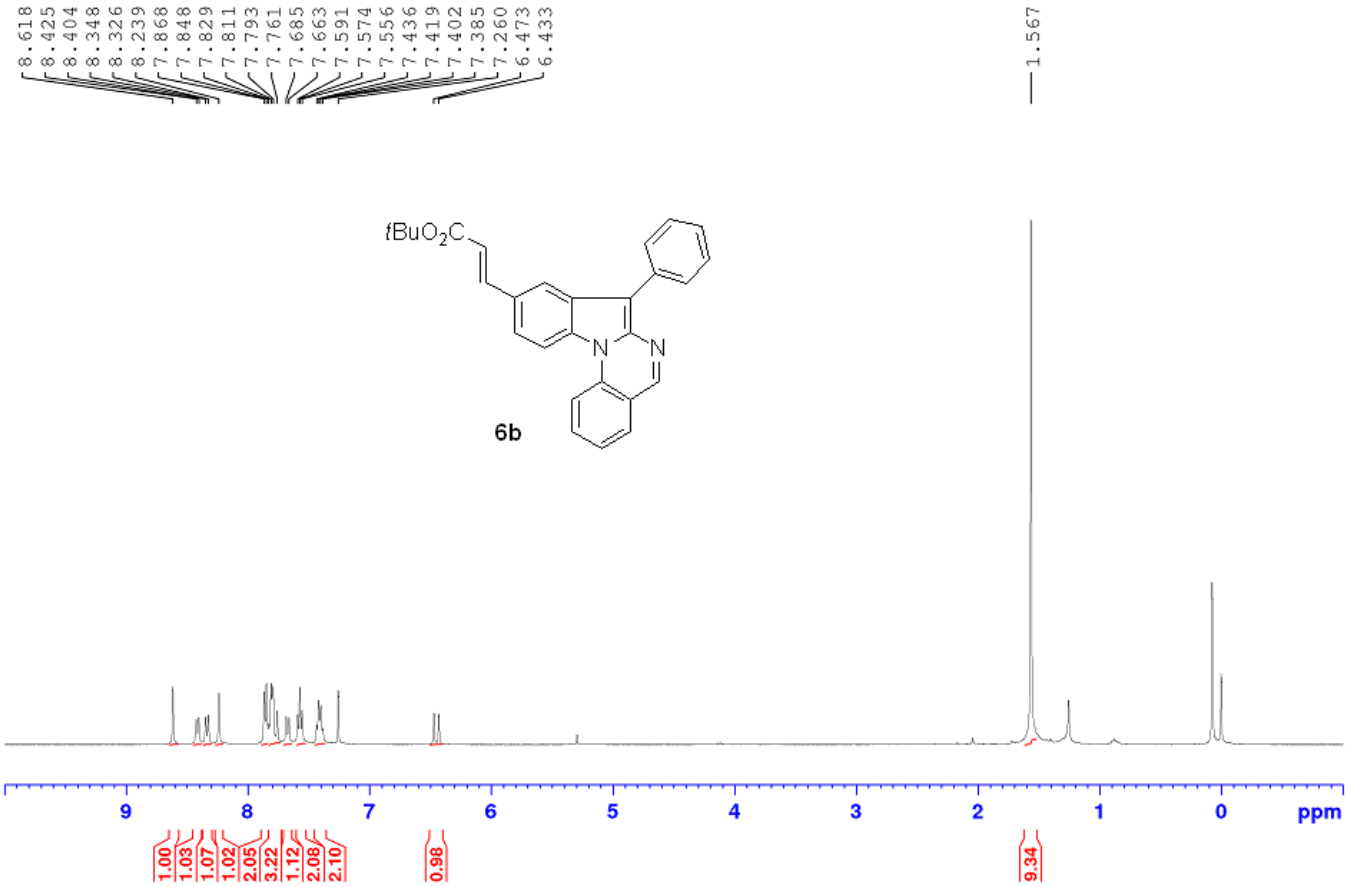


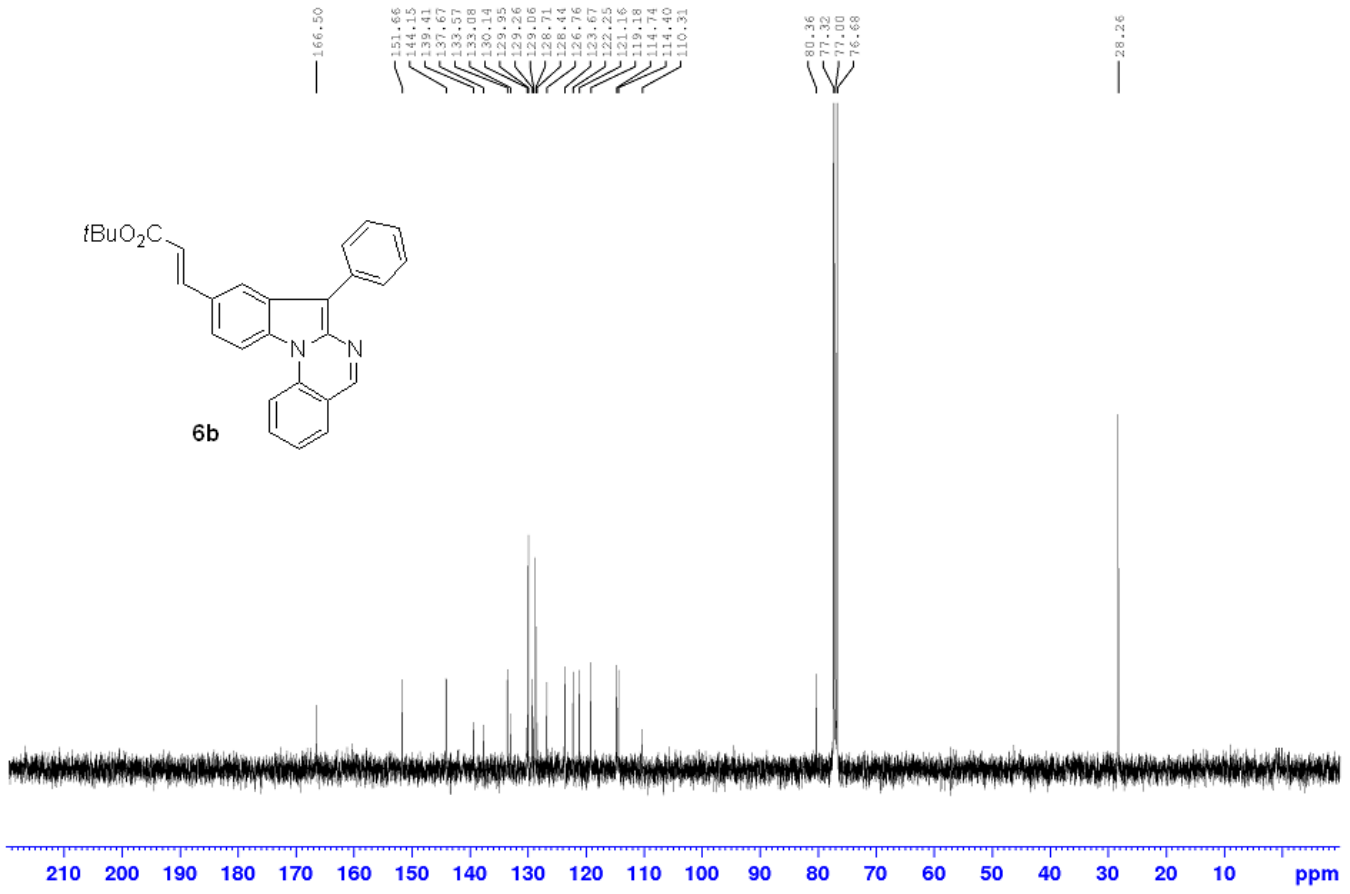
9-Bromo-7-phenylindolo[1,2-*a*]quinazoline (6a)



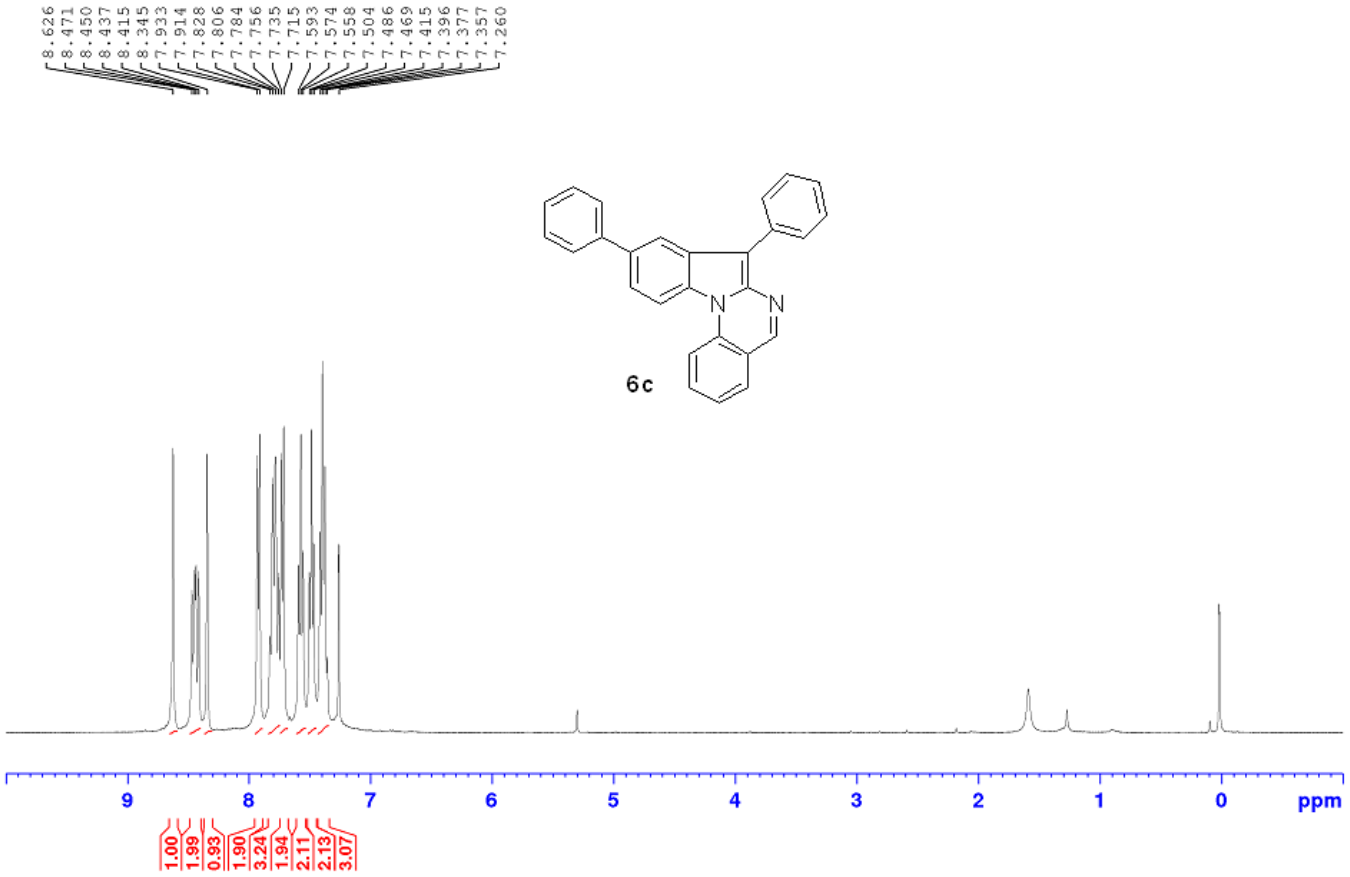


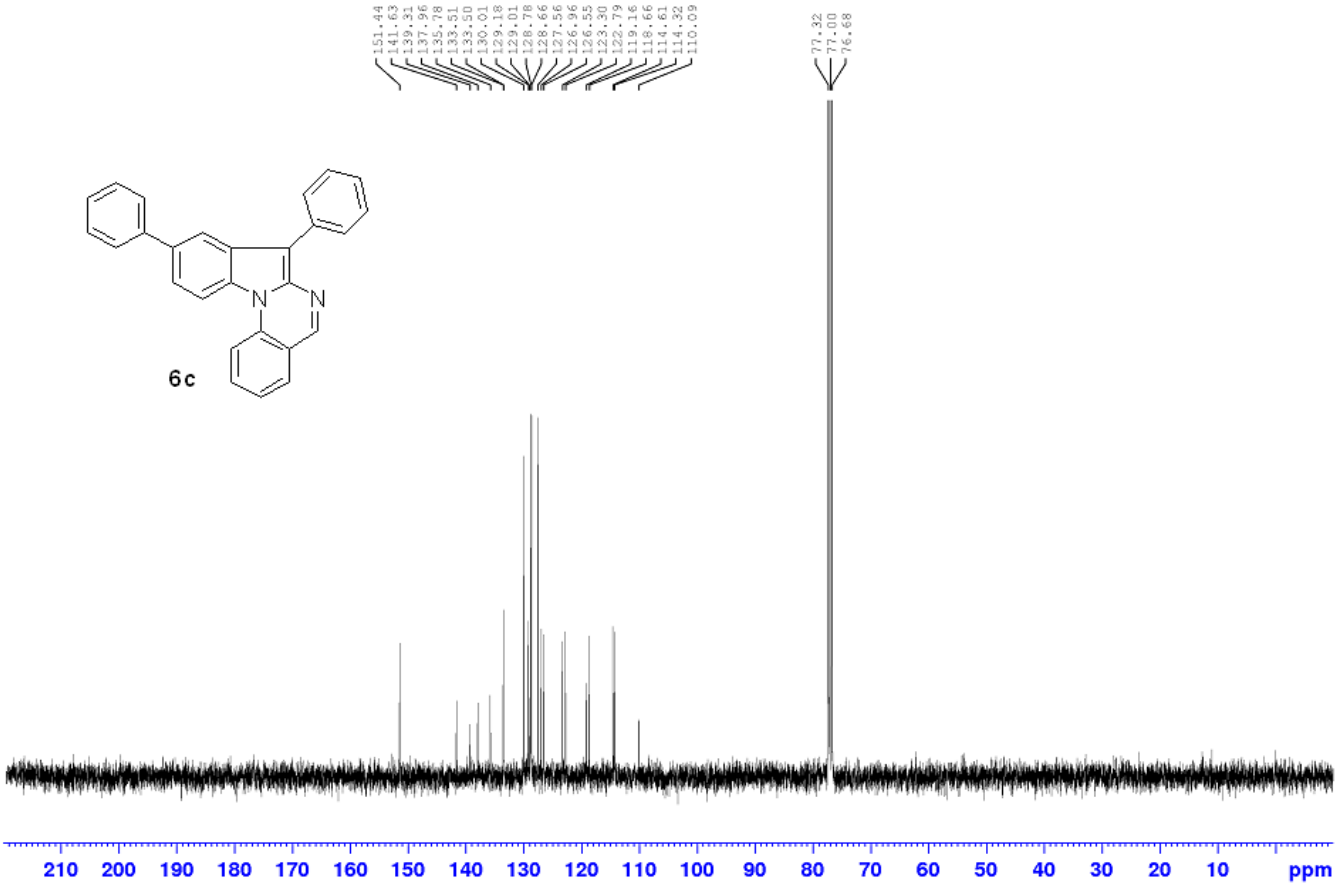
***tert*-Butyl (*E*)-3-(7-Phenylindolo[1,2-*a*]quinazolin-9-yl)acrylate (6b)**



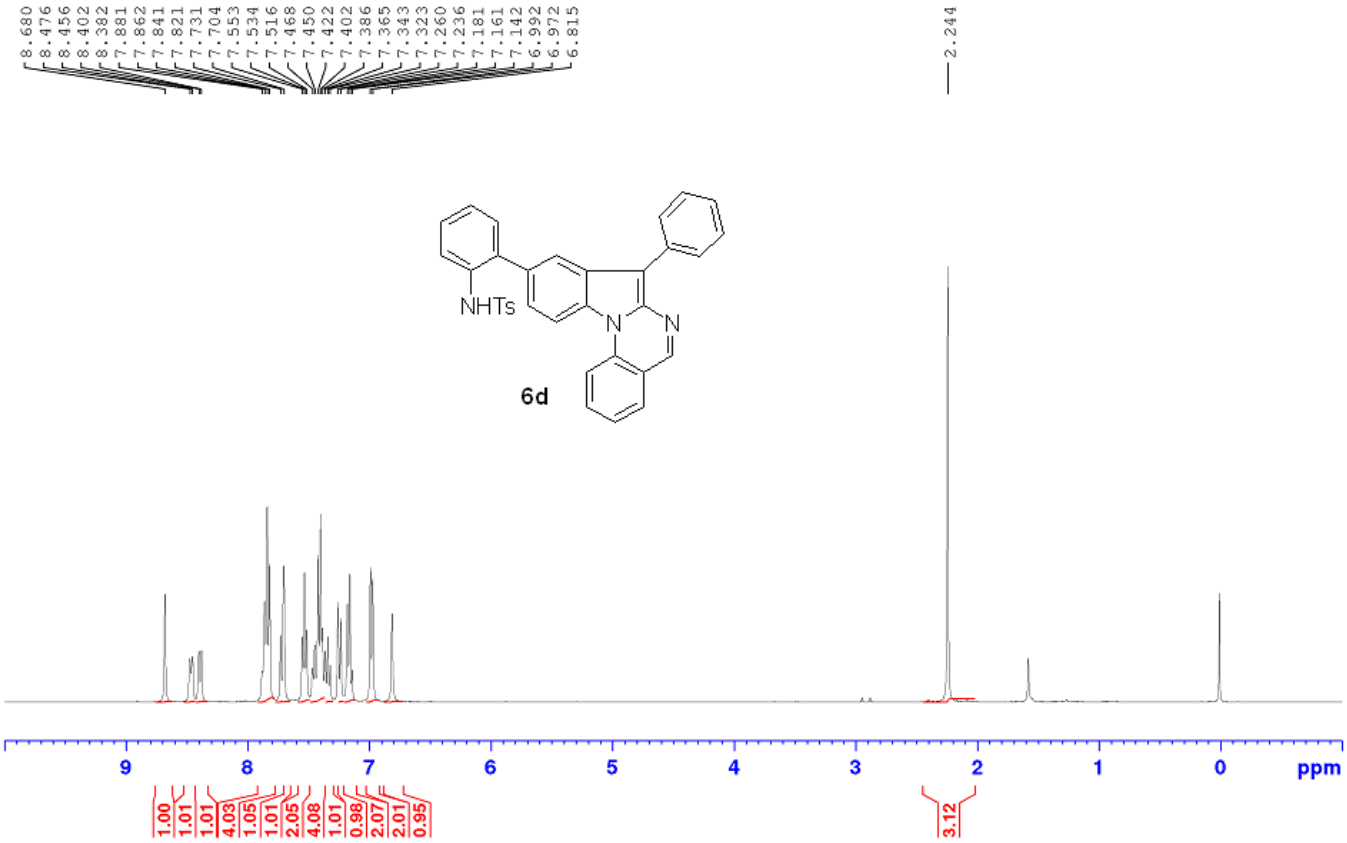


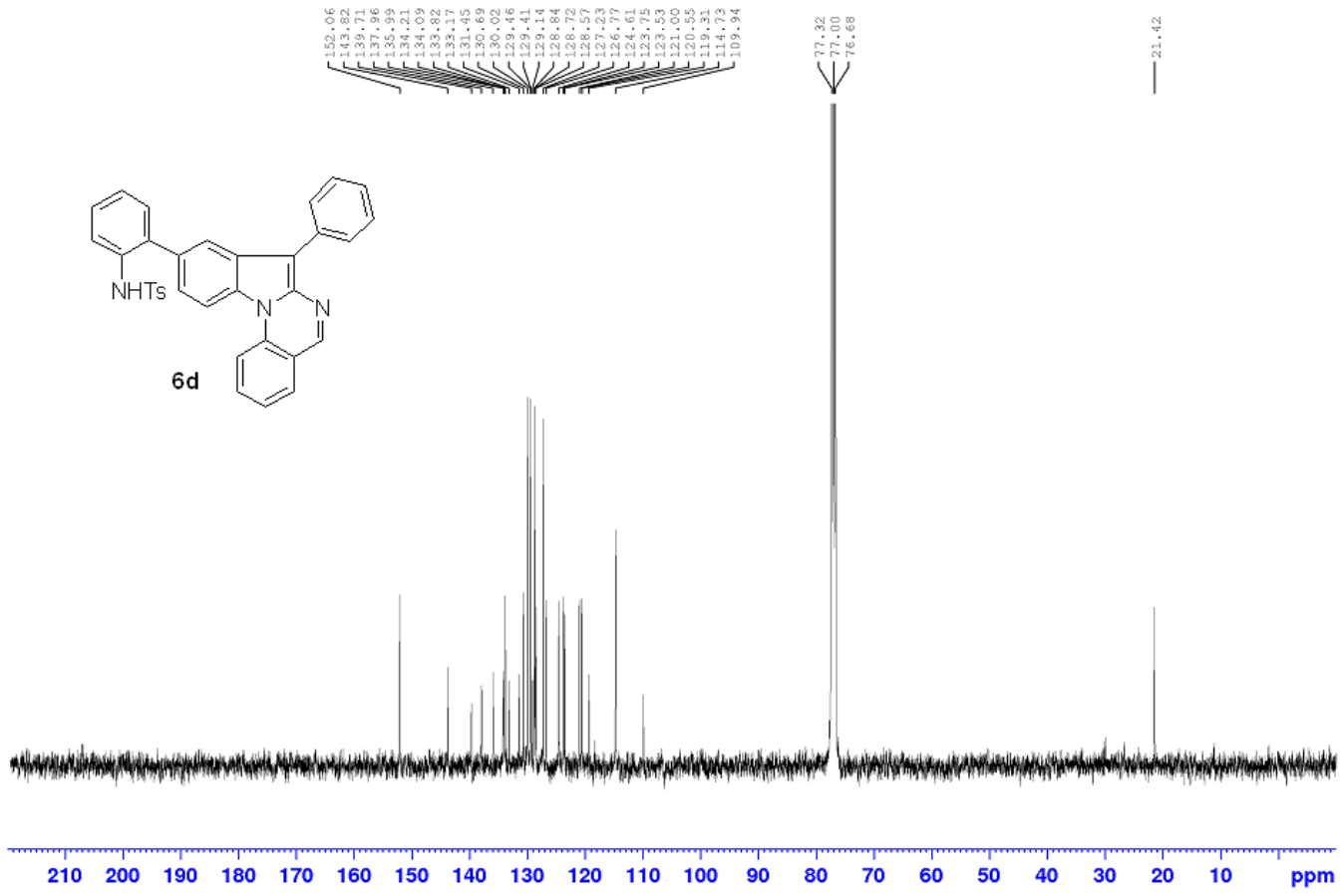
7,9-Diphenylindolo[1,2-*a*]quinazoline (6c)



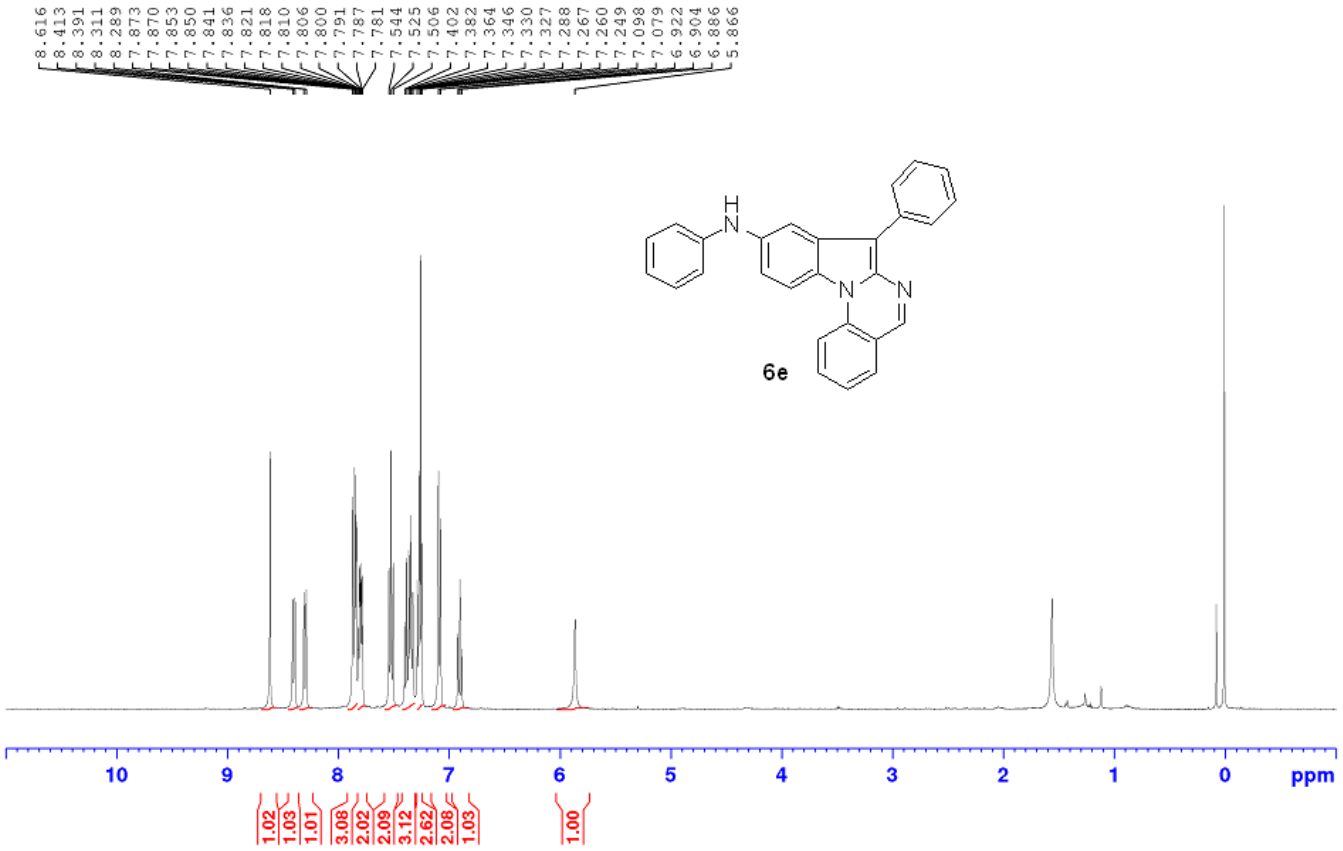


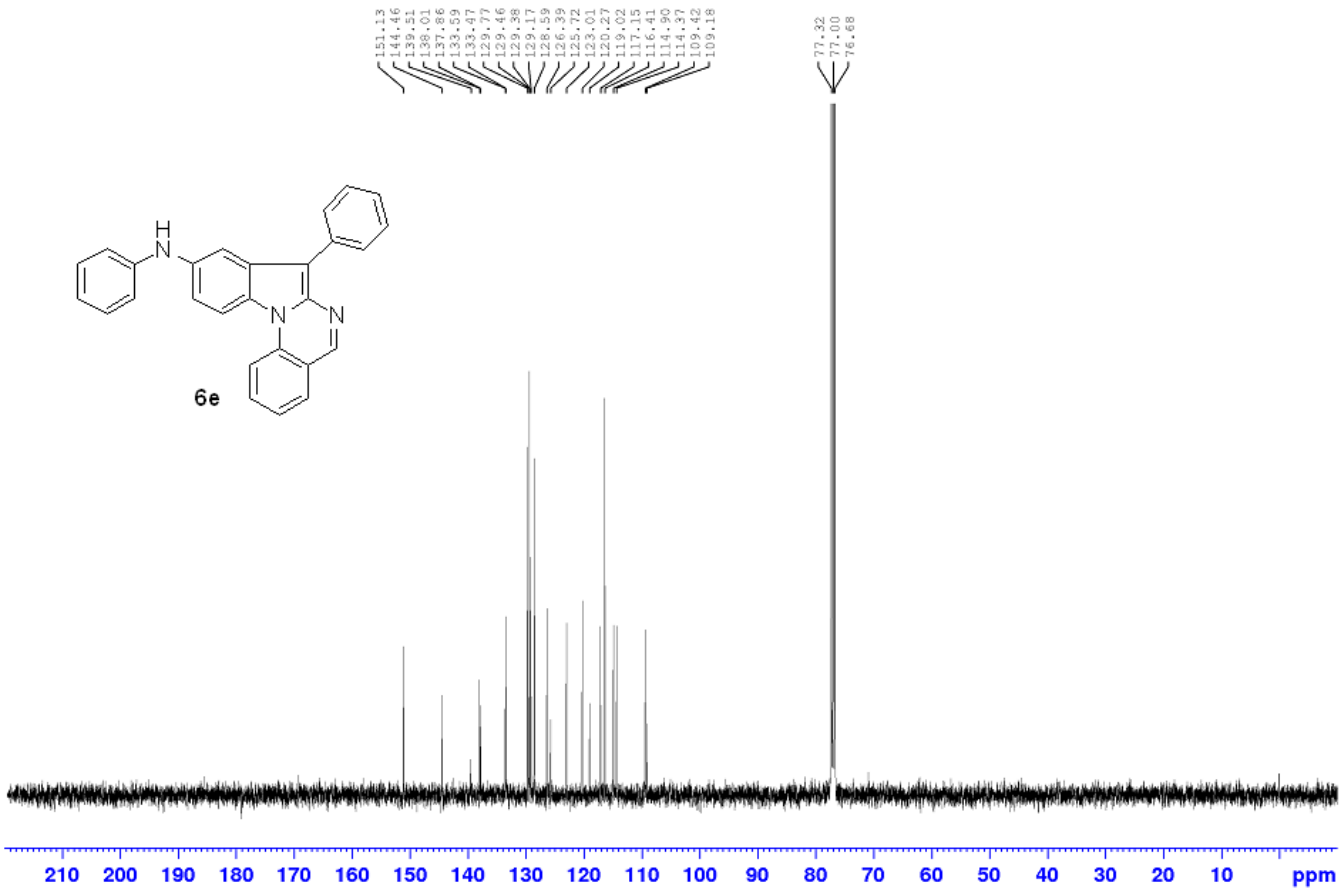
4-Methyl-*N*-(2-(7-phenylindolo[1,2-*a*]quinazolin-9-yl)phenyl)benzenesulfonamide (6d)



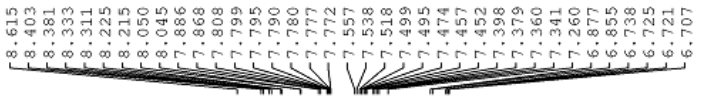


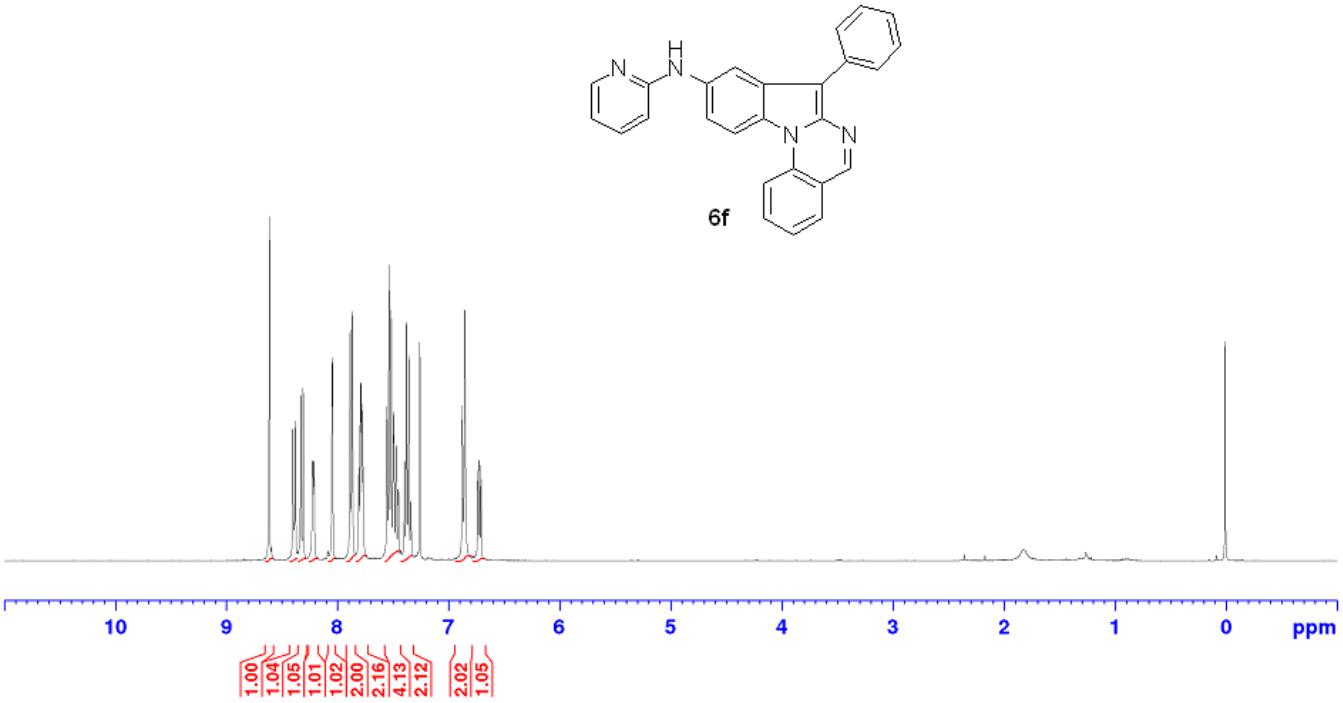
***N*,7-Diphenylindolo[1,2-*a*]quinazolin-9-amine (6e)**

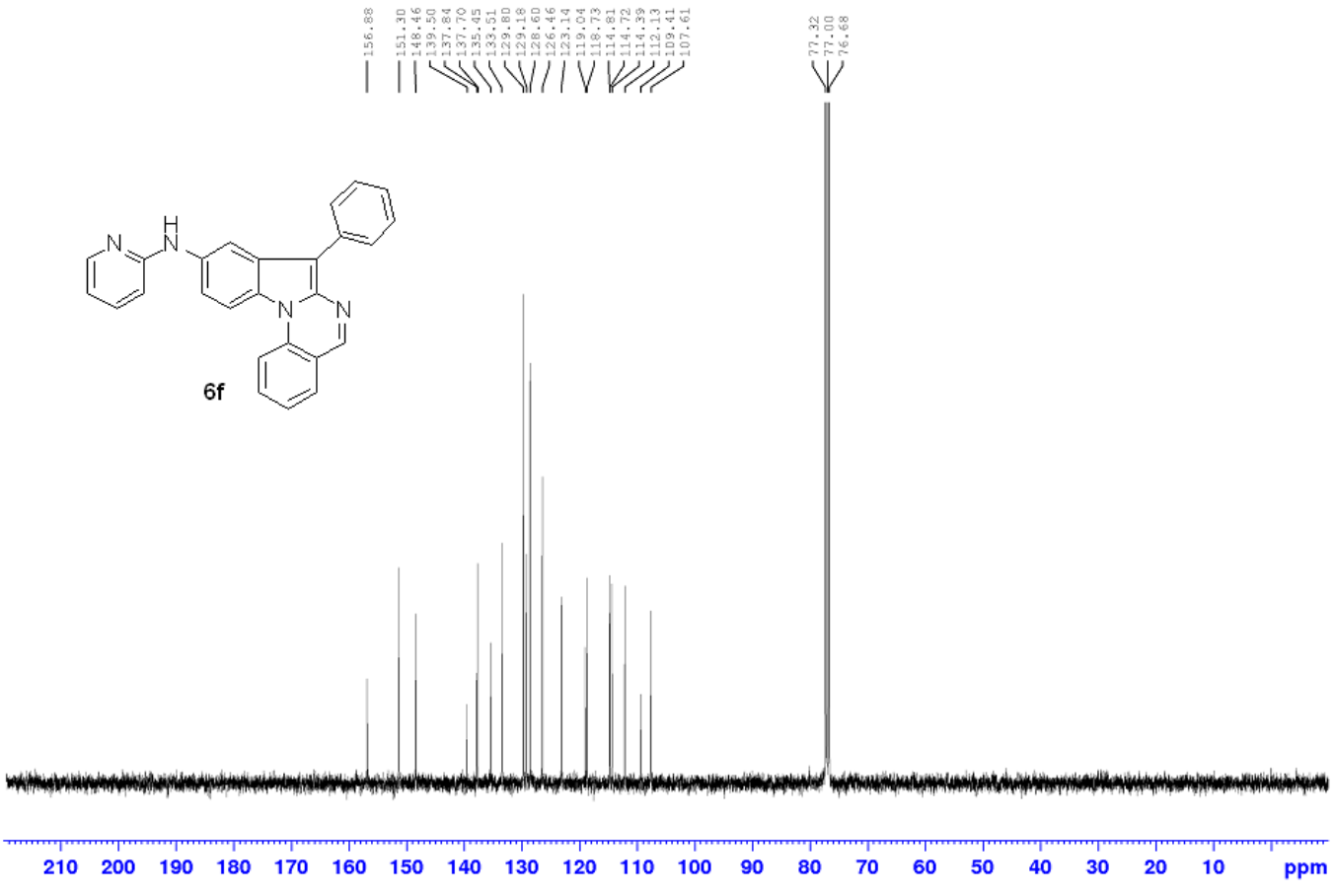




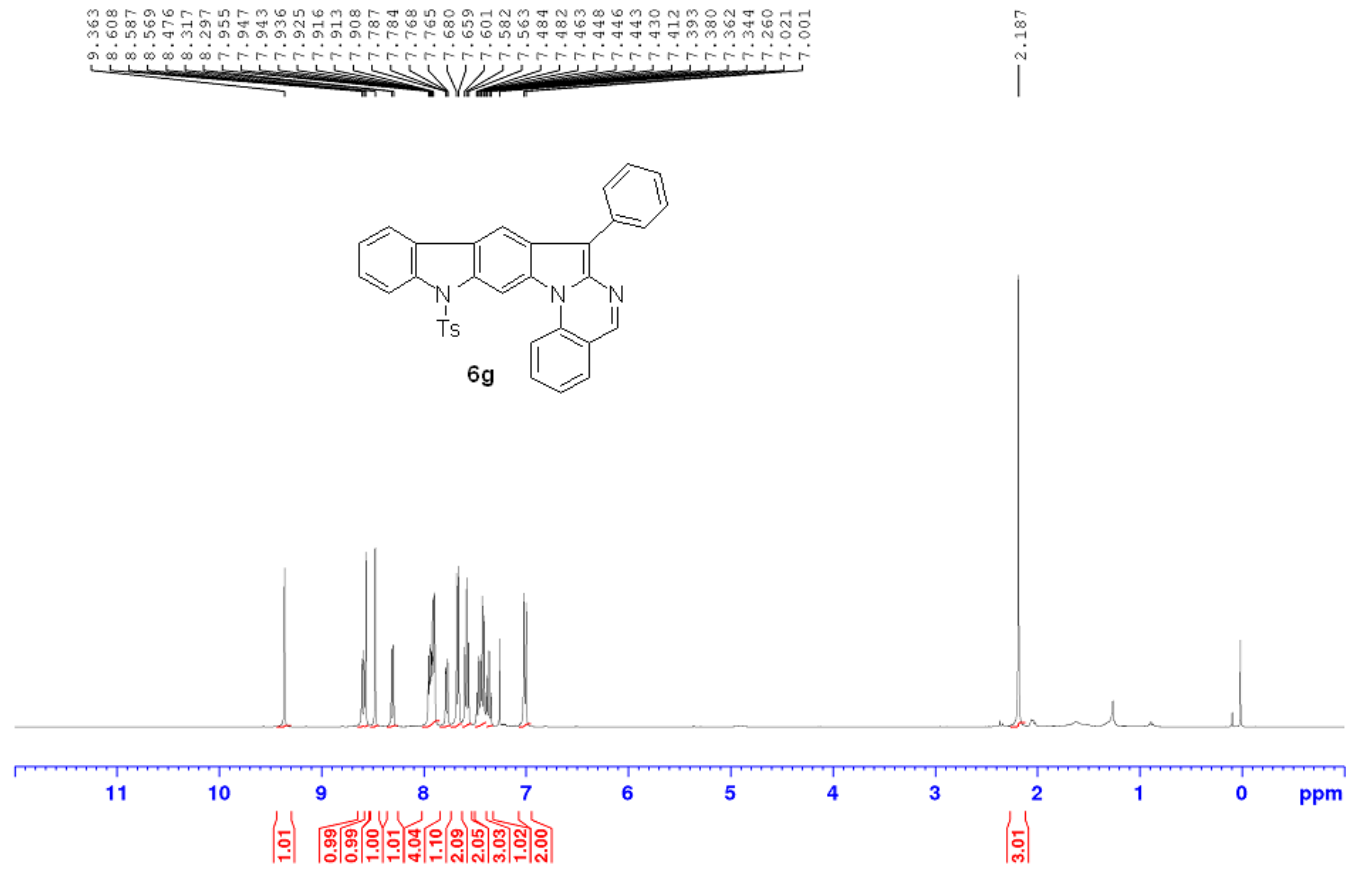
7-Phenyl-*N*-(pyridin-2-yl)indolo[1,2-*a*]quinazolin-9-amine (6f)

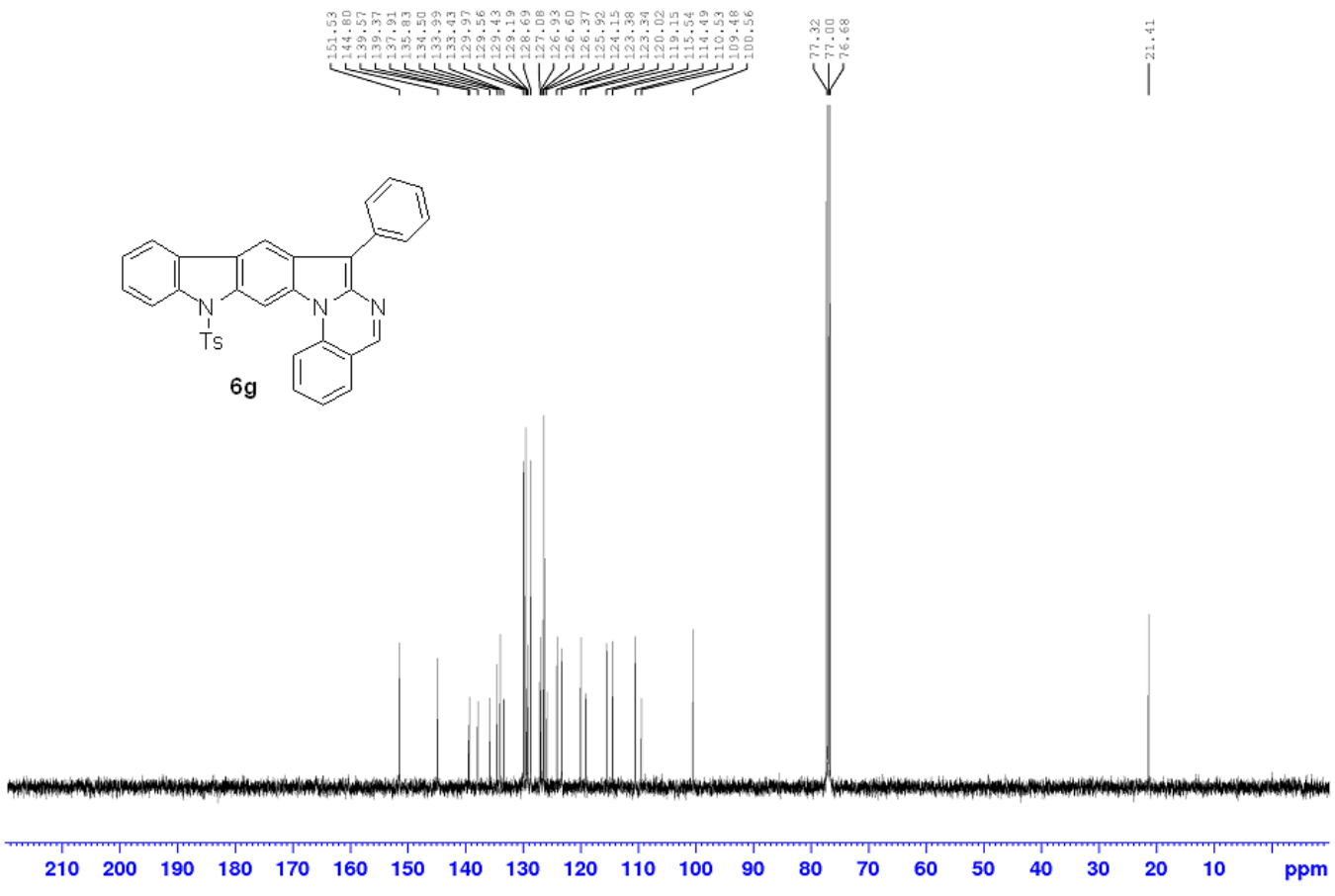




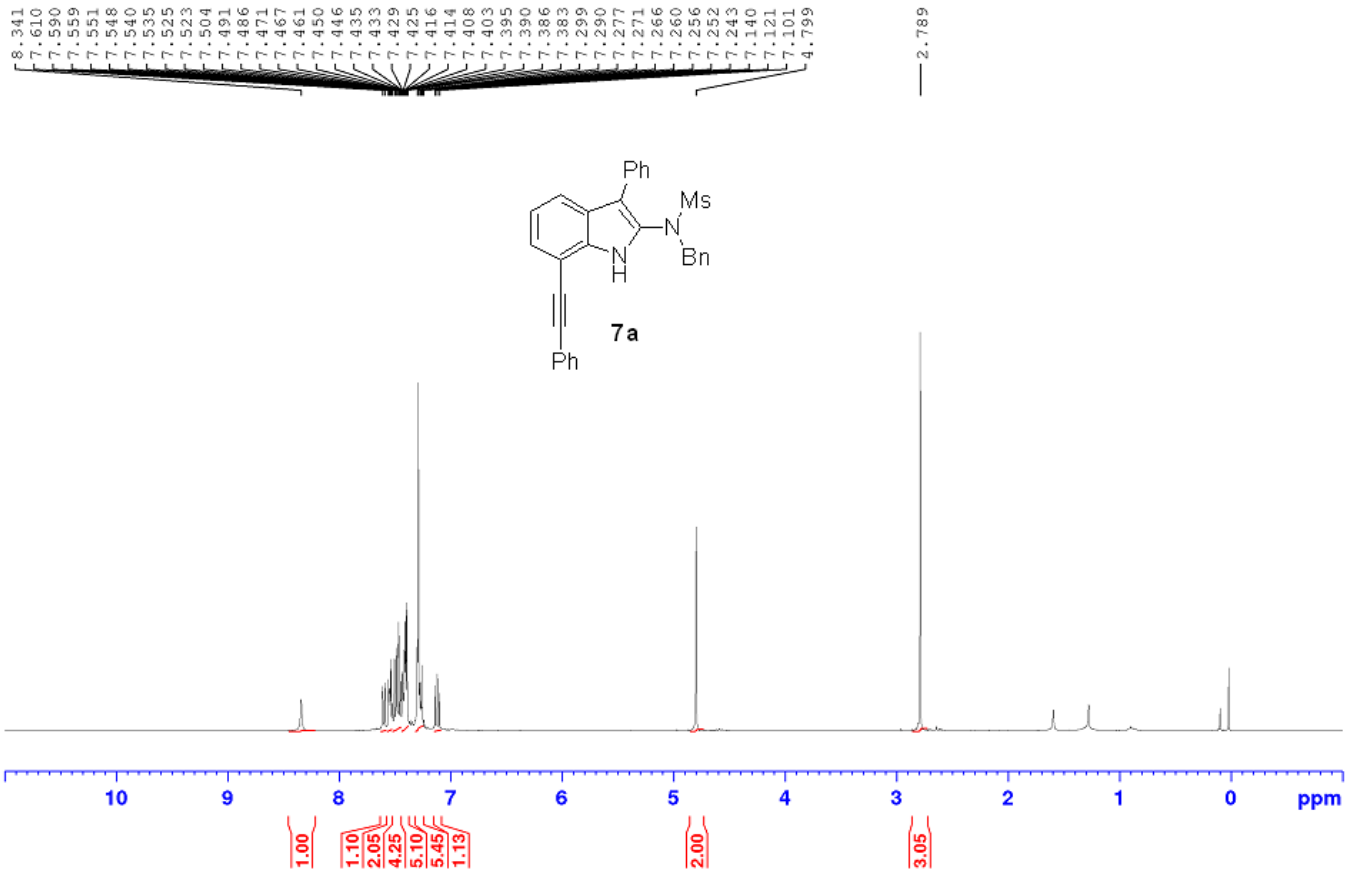


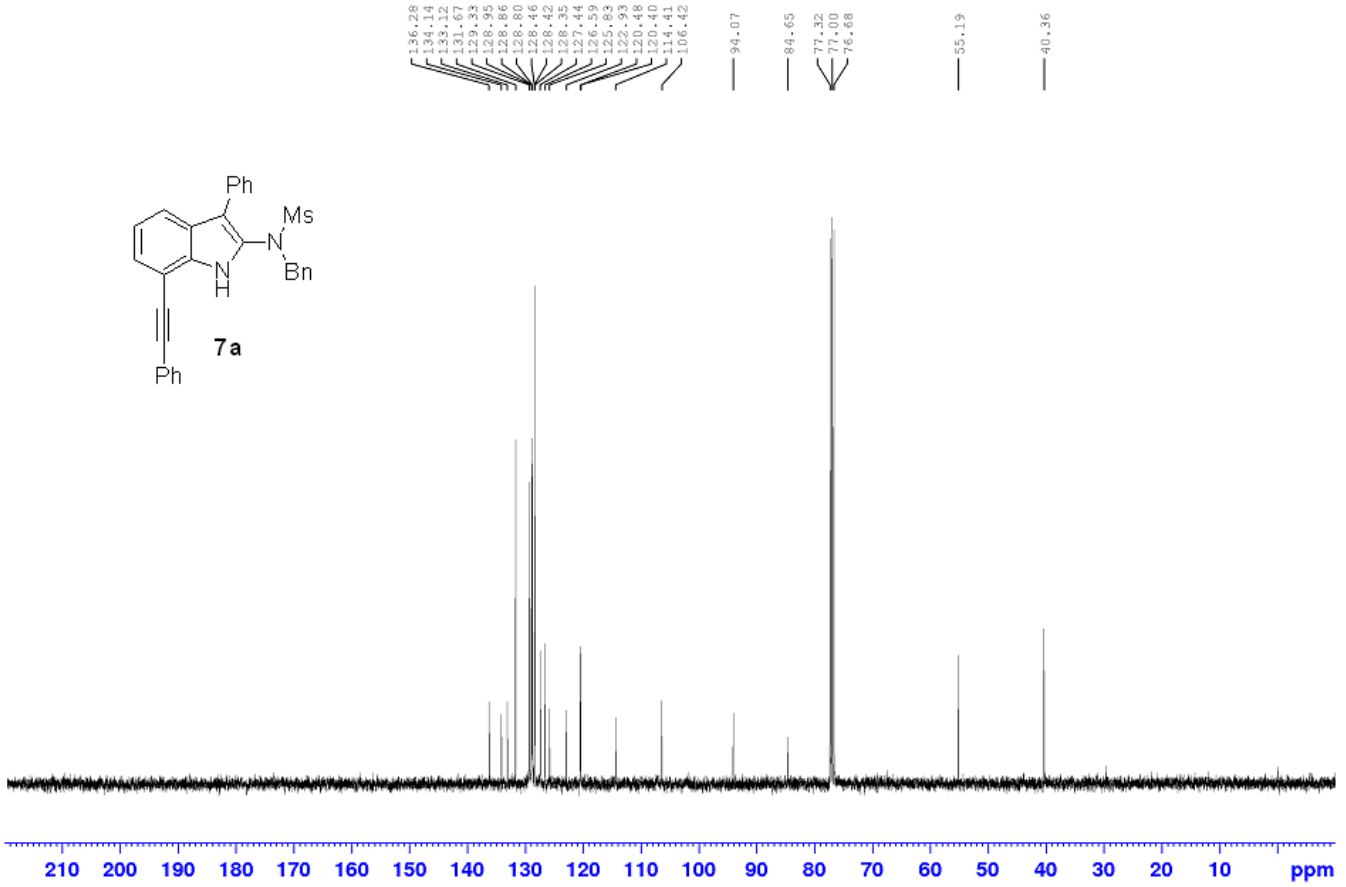
7-Phenyl-13-tosyl-13*H*-quinazolino[1',2':1,5]pyrrolo[2,3-*b*]carbazole (6g)



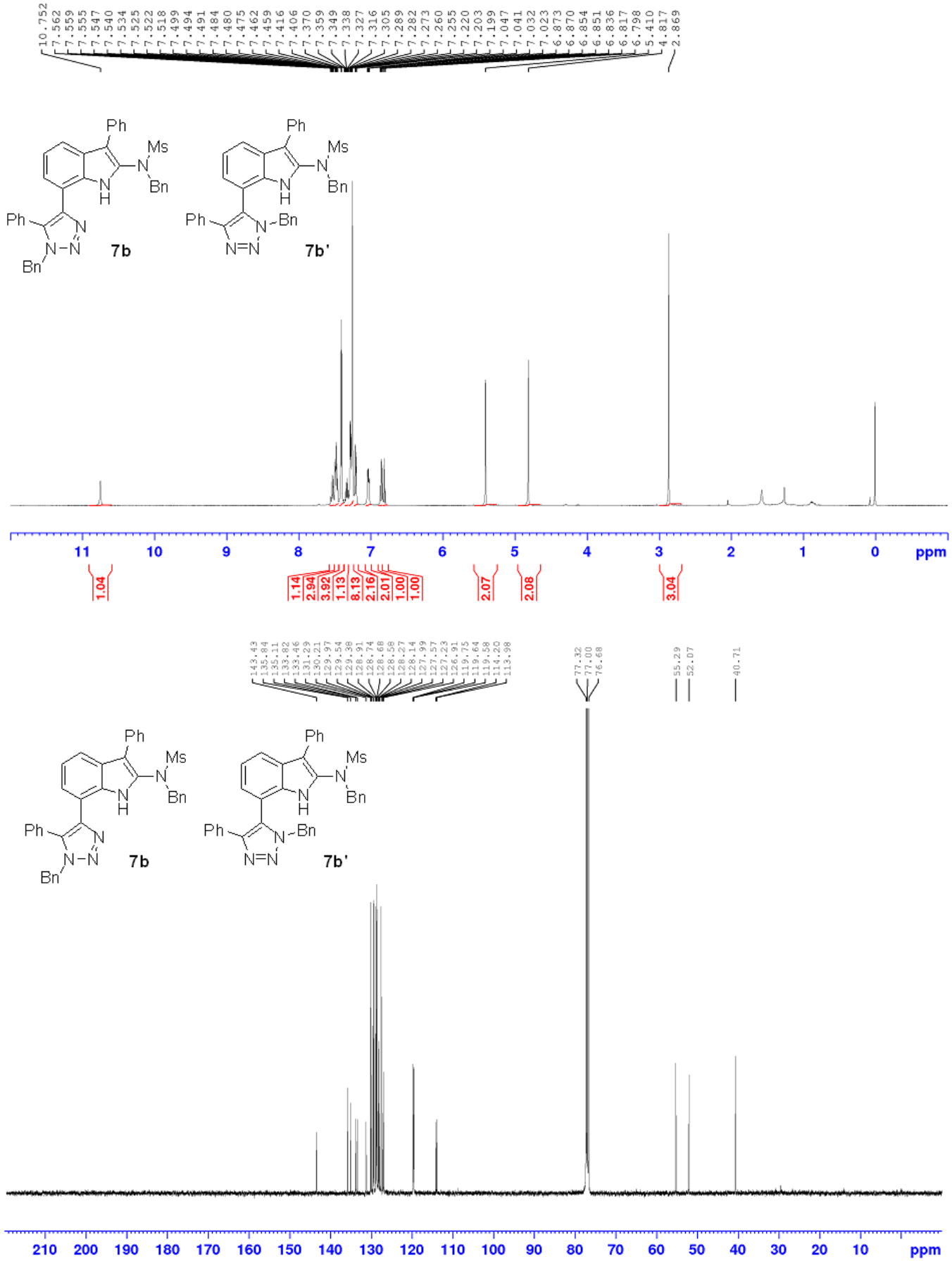


_N_-Benzyl-_N_-(3-phenyl-7-(phenylethynyl)-1_H_-indol-2-yl)methanesulfonamide (7a)

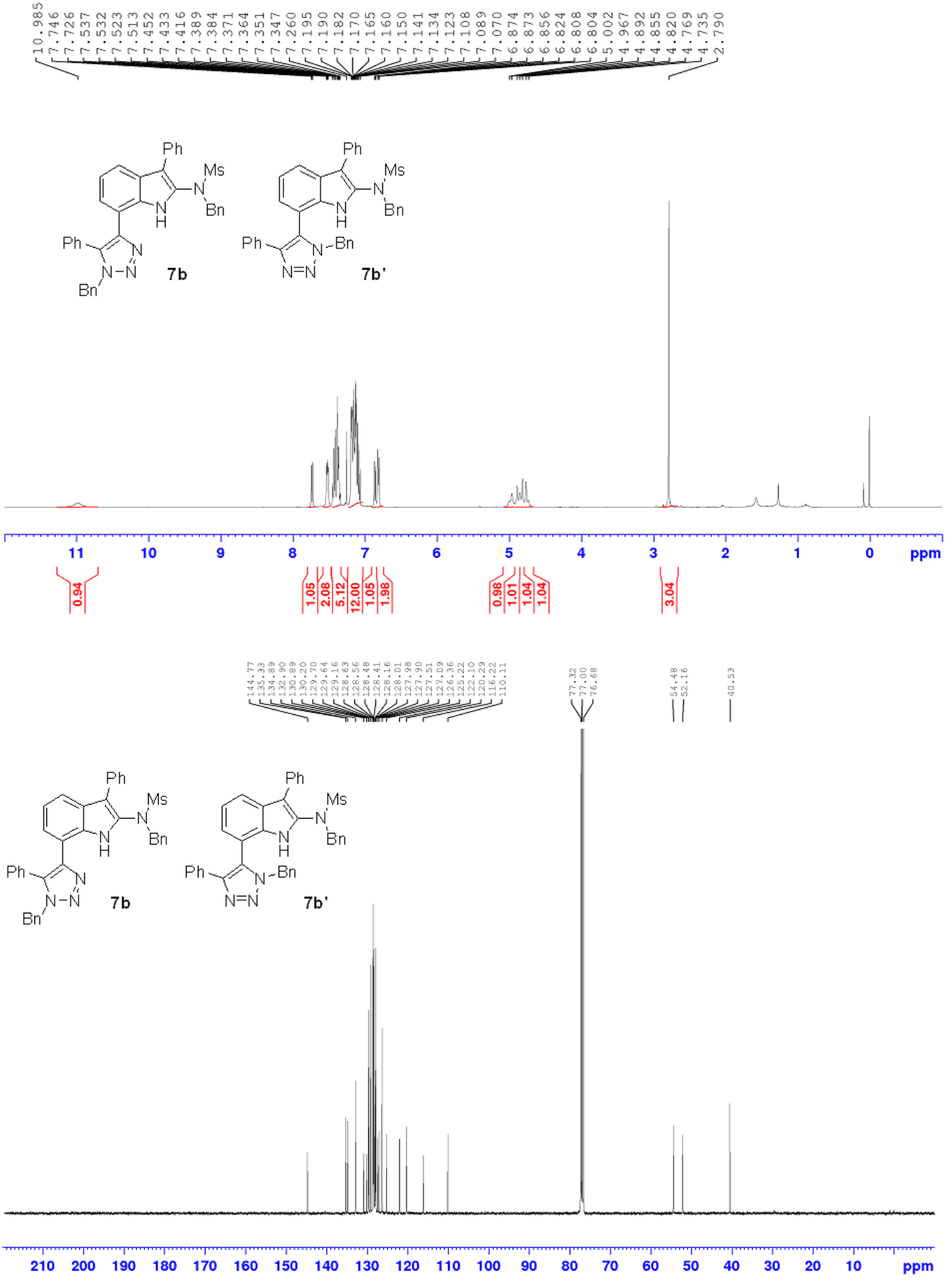




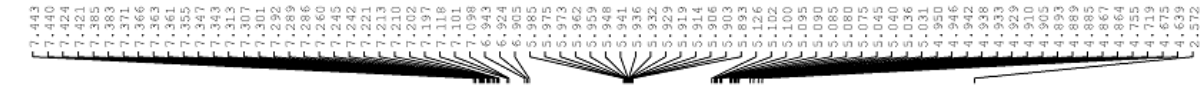
_N_-Benzyl-_N_-(7-(1-benzyl-5-phenyl-1_H_-1,2,3-triazol-4-yl)-3-phenyl-1_H_-indol-2-yl)methanesulfonamide (7b) & _N_-Benzyl-_N_-(7-(1-benzyl-4-phenyl-1_H_-1,2,3-triazol-5-yl)-3-phenyl-1_H_-indol-2-yl)methanesulfonamide (7b′) - A

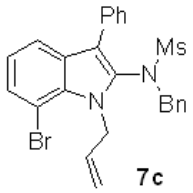


_N_-Benzyl-_N_-(7-(1-benzyl-5-phenyl-1_H_-1,2,3-triazol-4-yl)-3-phenyl-1_H_-indol-2-yl)methanesulfonamide (7b) & _N_-Benzyl-_N_-(7-(1-benzyl-4-phenyl-1_H_-1,2,3-triazol-5-yl)-3-phenyl-1_H_-indol-2-yl)methanesulfonamide (7b′) - B

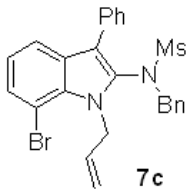


***N*-(1-Allyl-7-bromo-3-phenyl-1*H*-indol-2-yl)-*N*-benzylmethanesulfonamide (7c)**

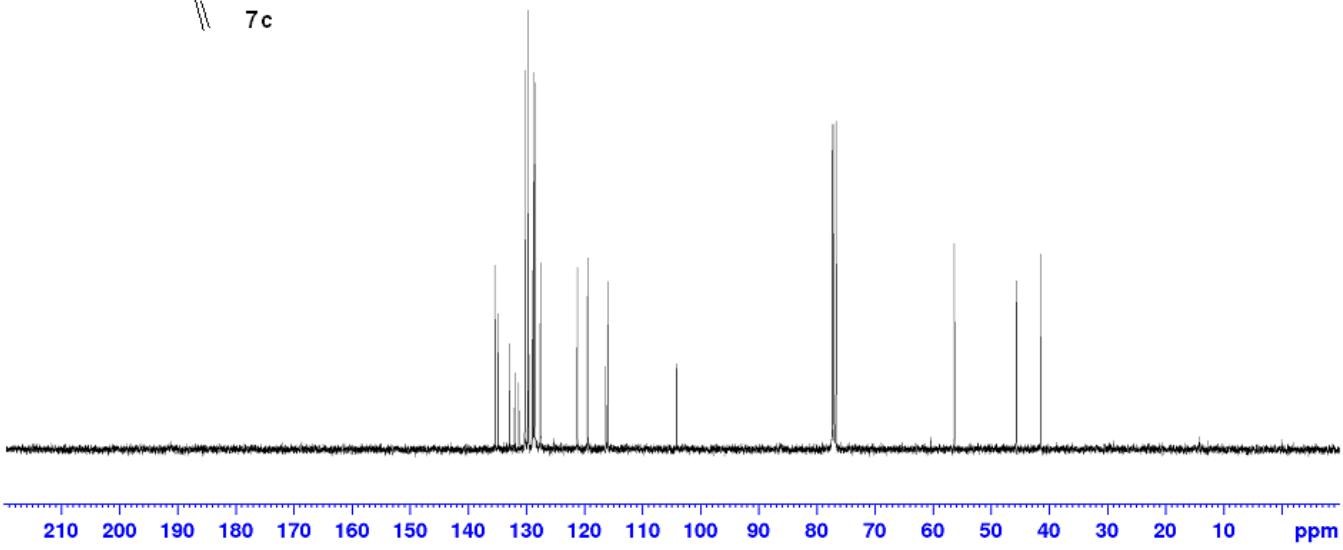




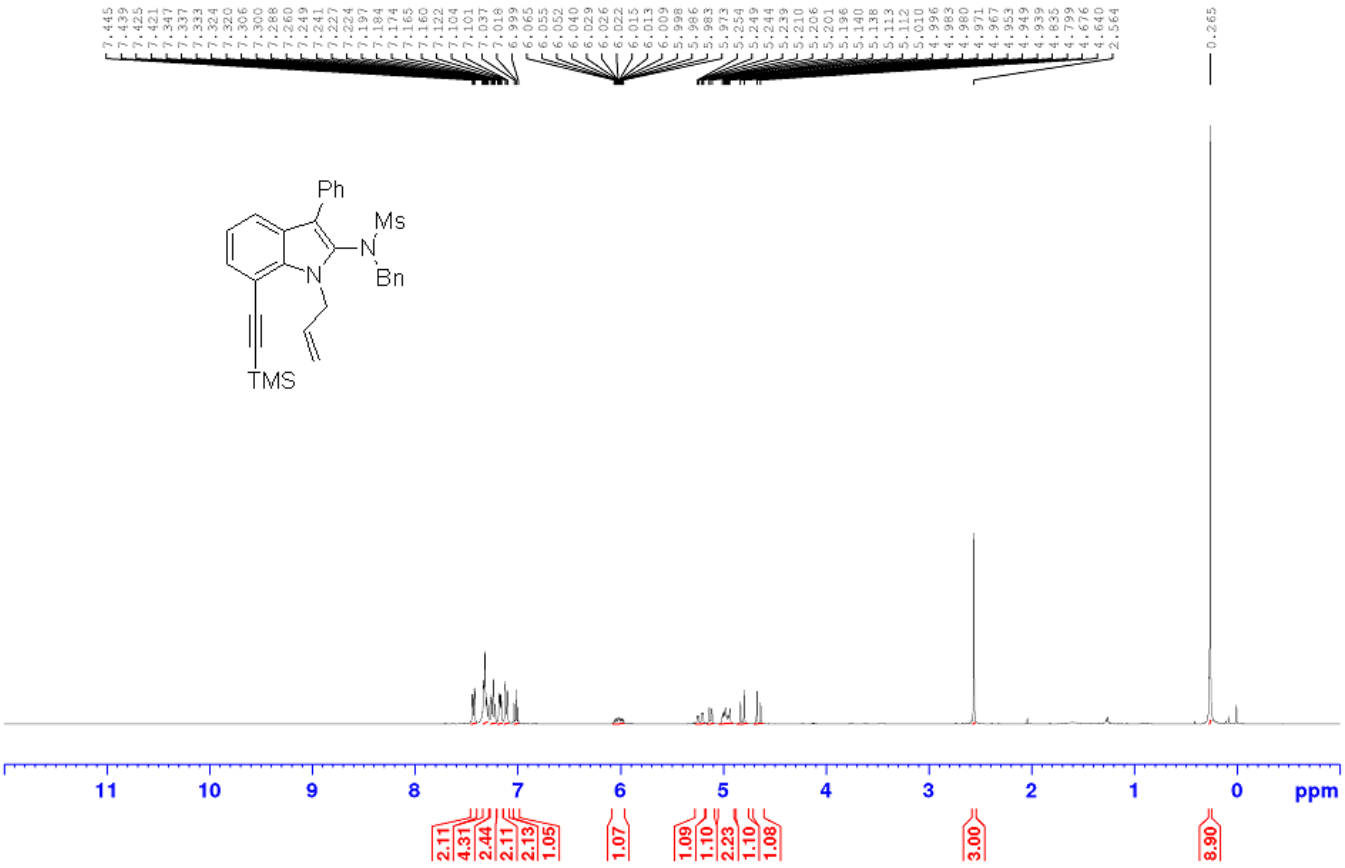
7c

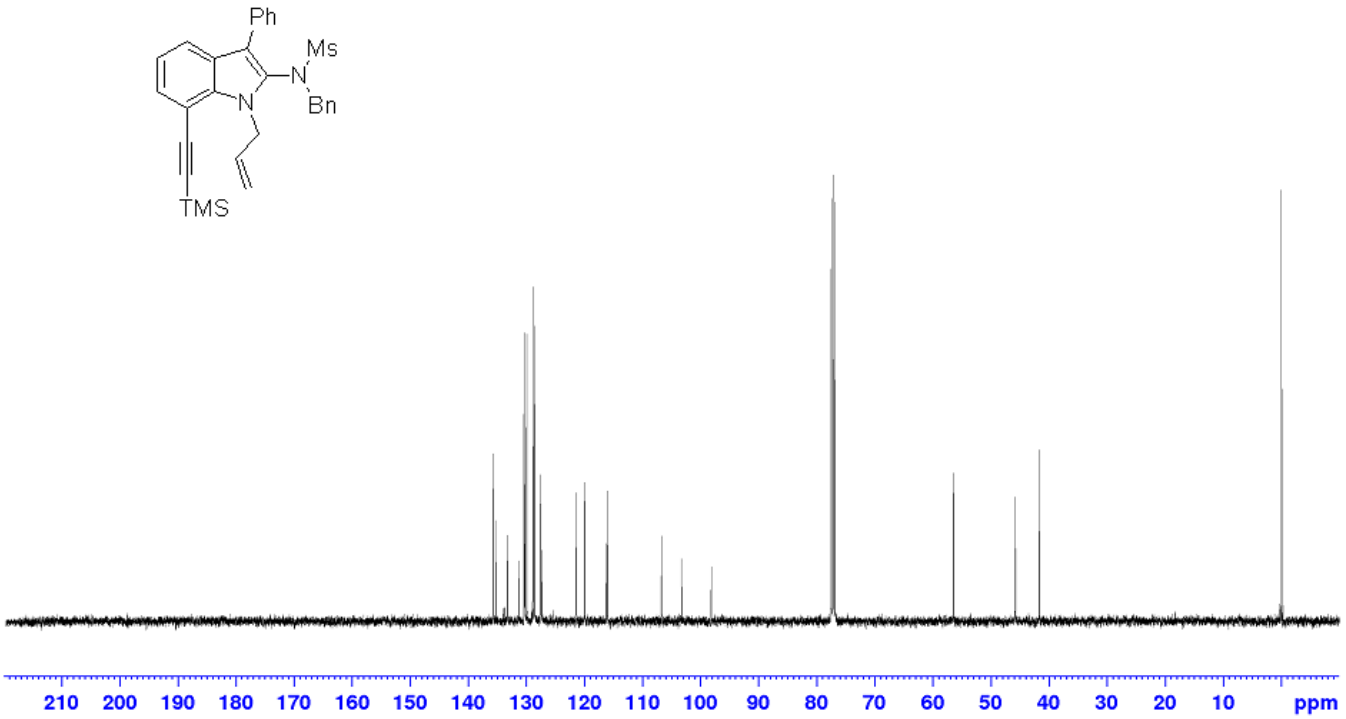


7c

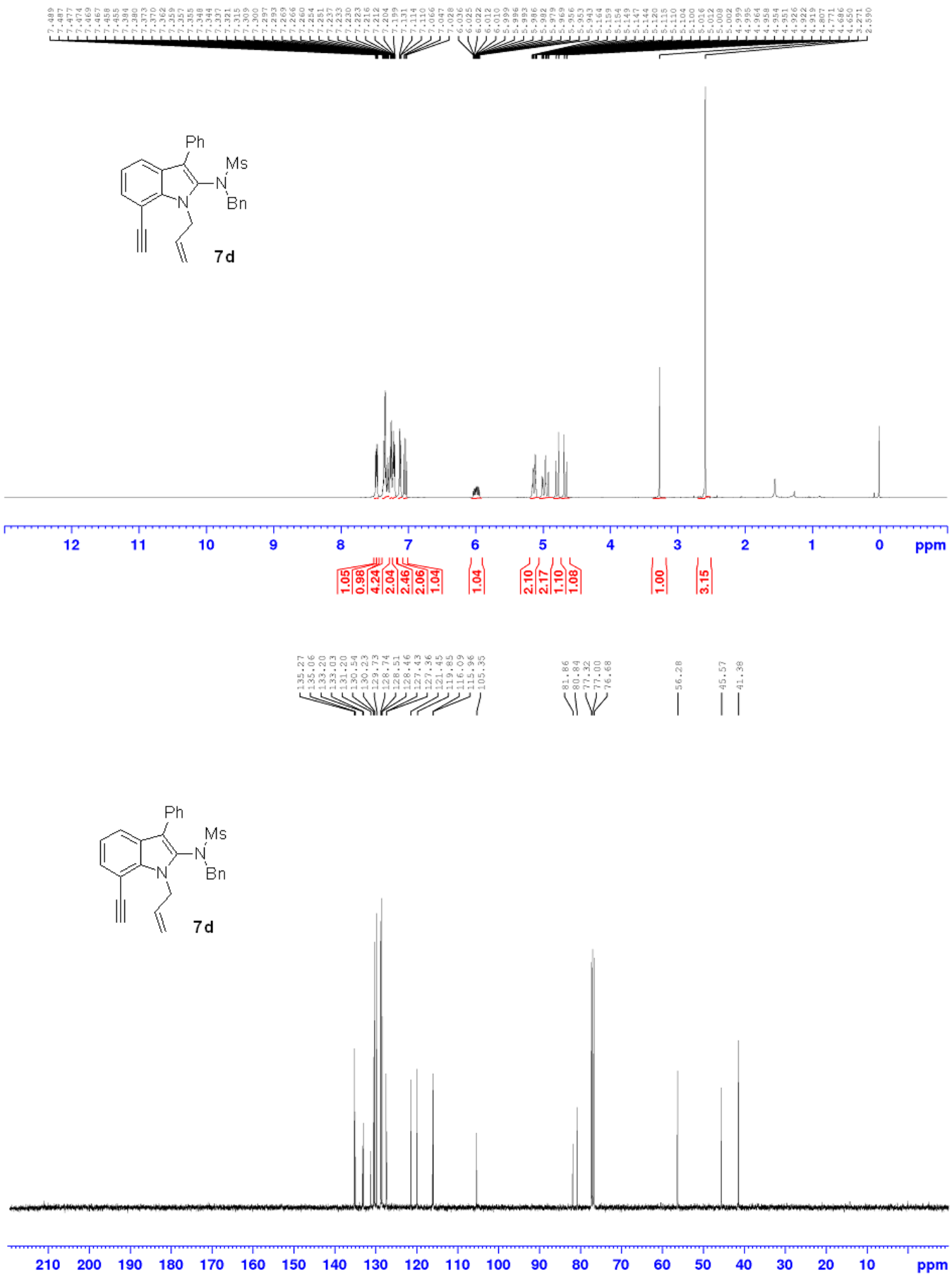


***N*-(1-Allyl-3-phenyl-7-((trimethylsilyl)ethynyl)-1*H*-indol-2-yl)-*N*-benzylmethanesulfonamide**

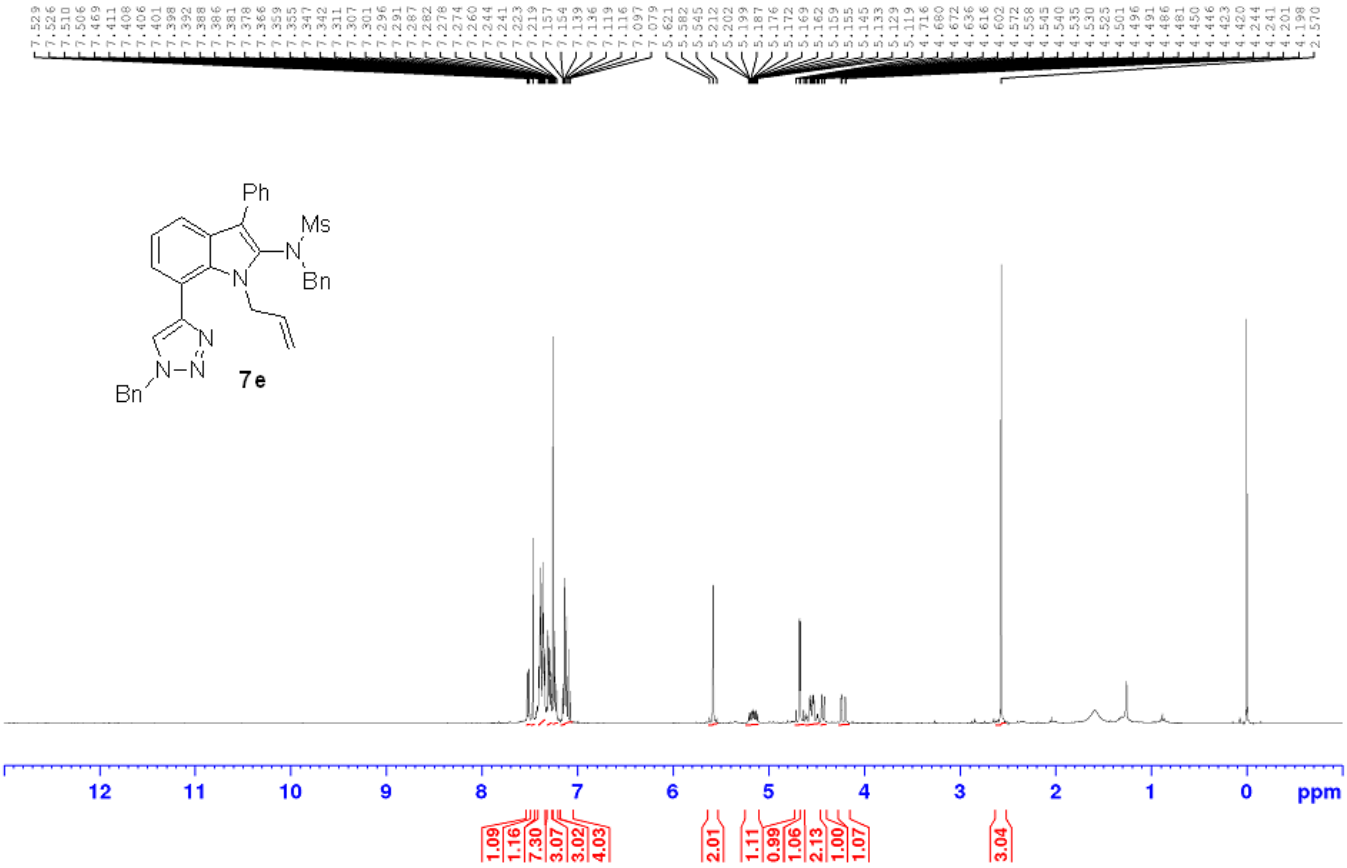


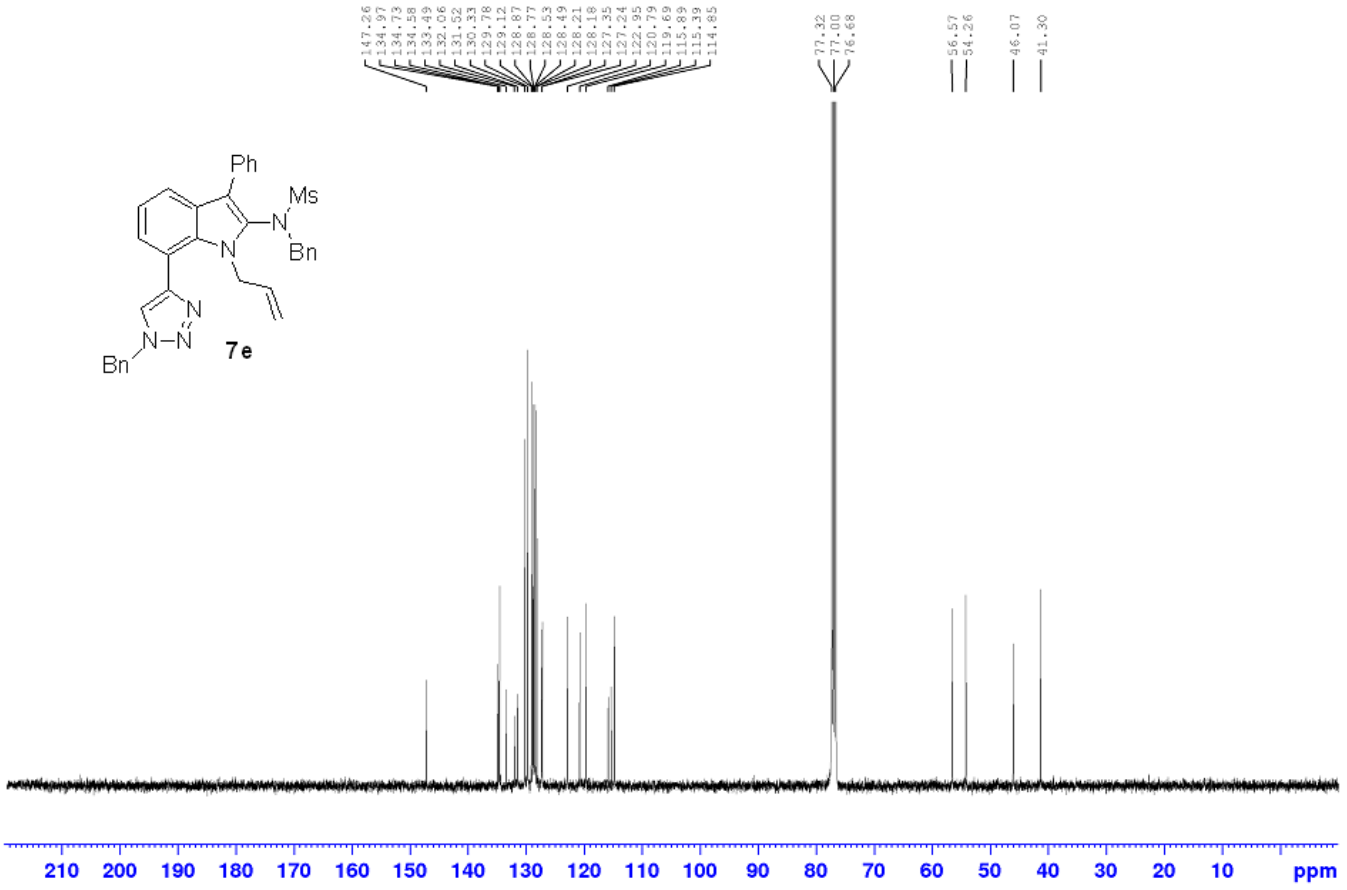


***N*-(1-Allyl-7-ethynyl-3-phenyl-1*H*-indol-2-yl)-*N*-benzylmethanesulfonamide (7d)**

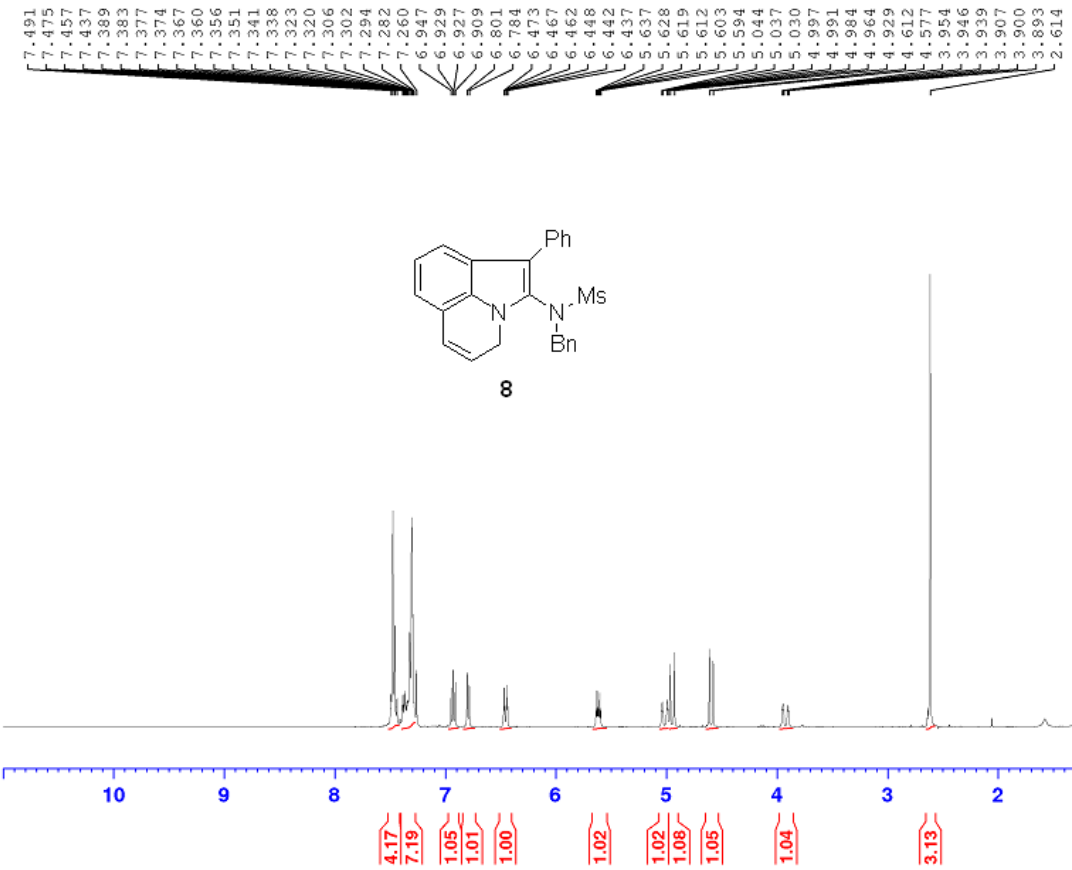


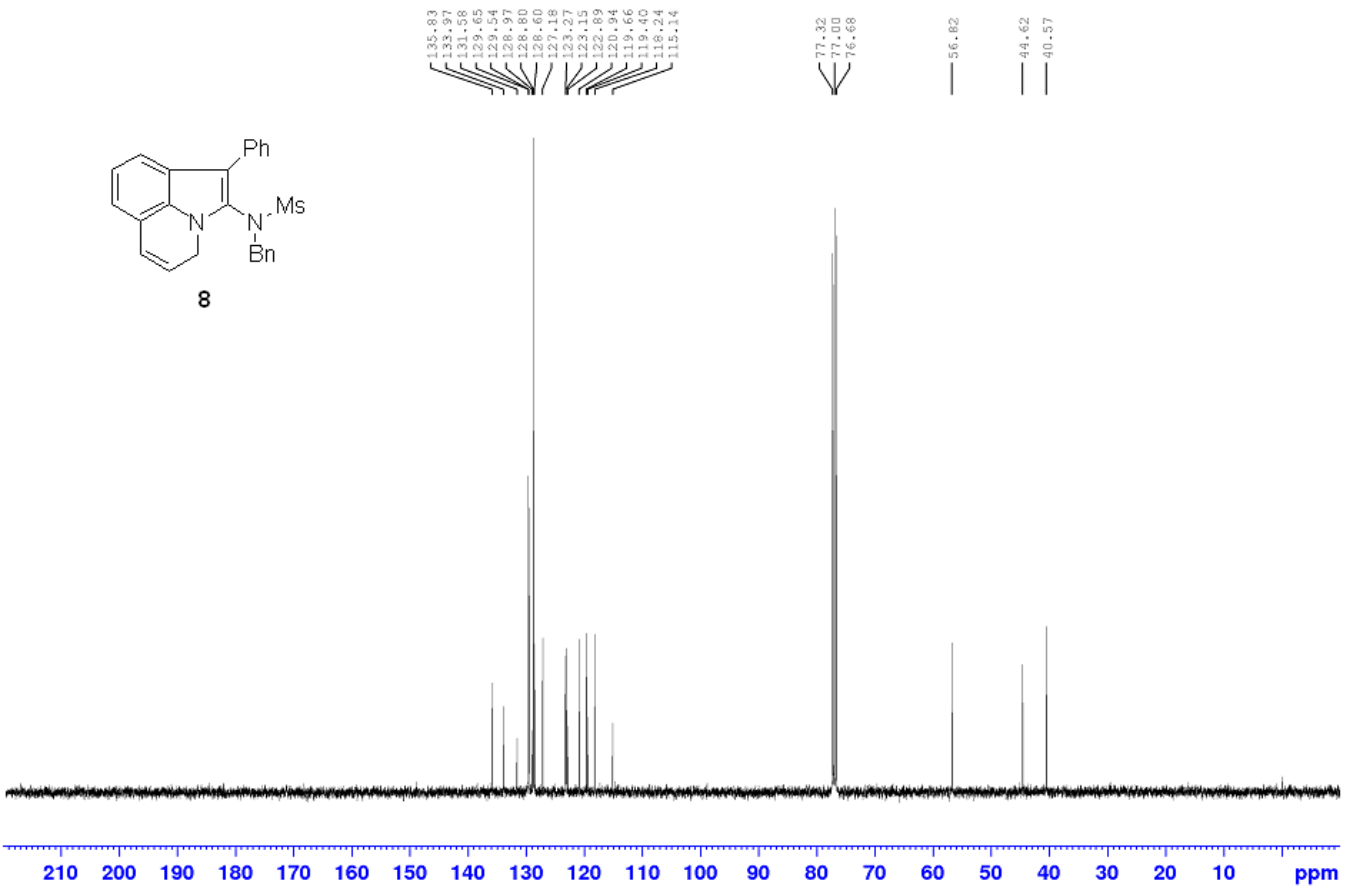
***N*-(1-Allyl-3-phenyl-7-(1-tosyl-1*H*-1,2,3-triazol-4-yl)-1*H*-indol-2-yl)-*N*-benzylmethanesulfonamide (7e)**



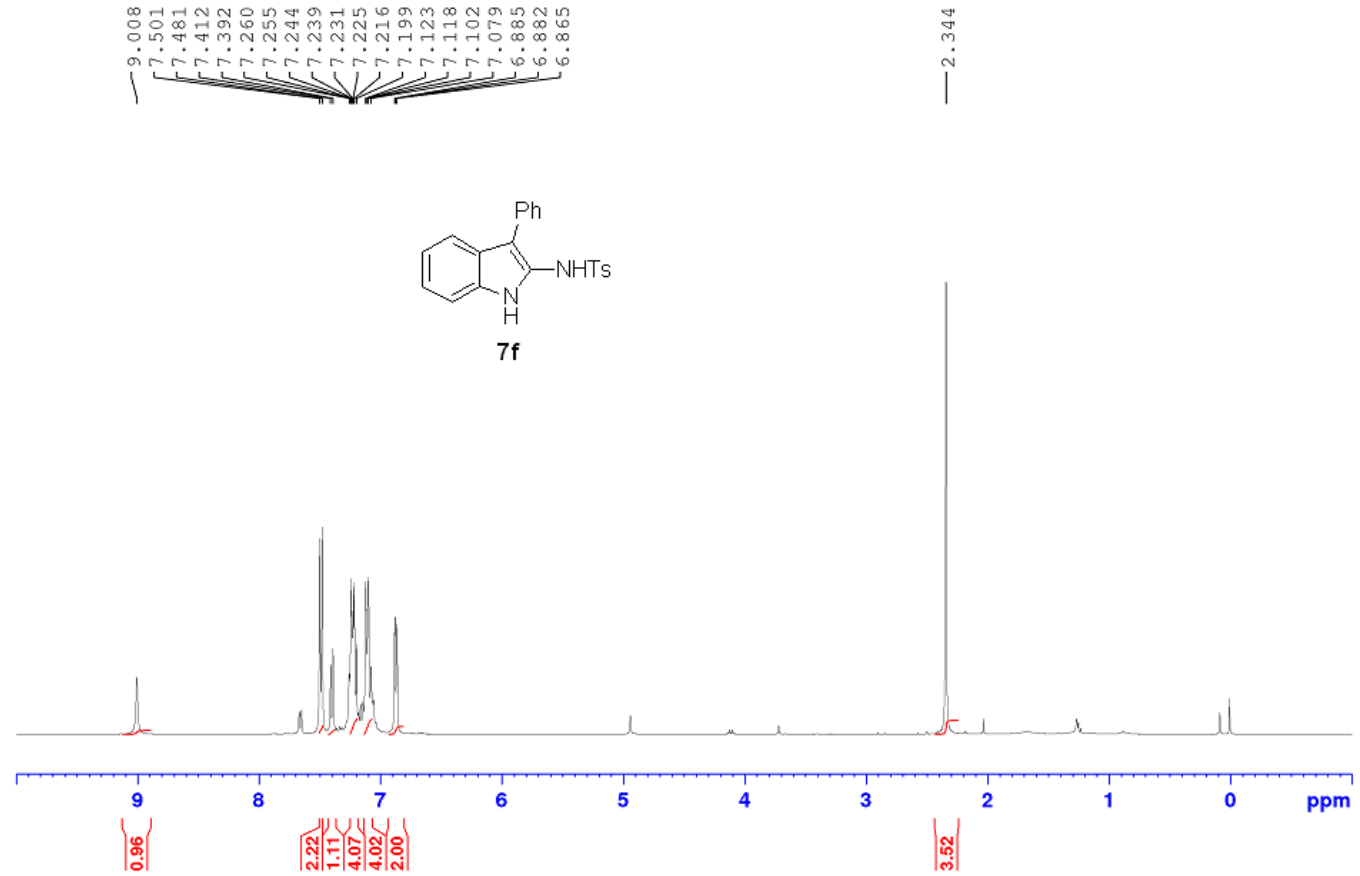


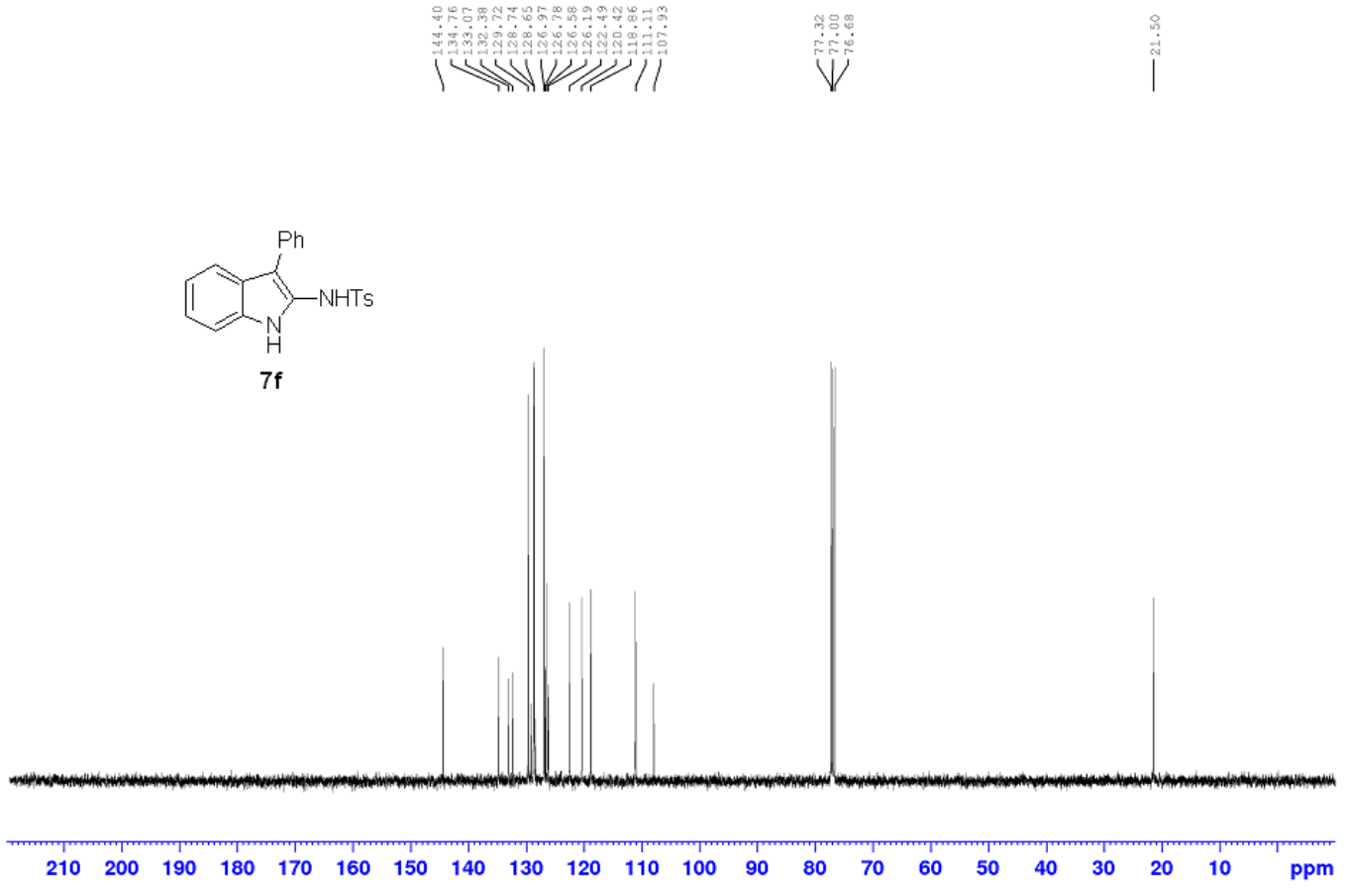
_N_-Benzyl-_N_-(1-phenyl-4_H_-pyrrolo[3,2,1-_ij_]quinolin-2-yl)methanesulfonamide (8)



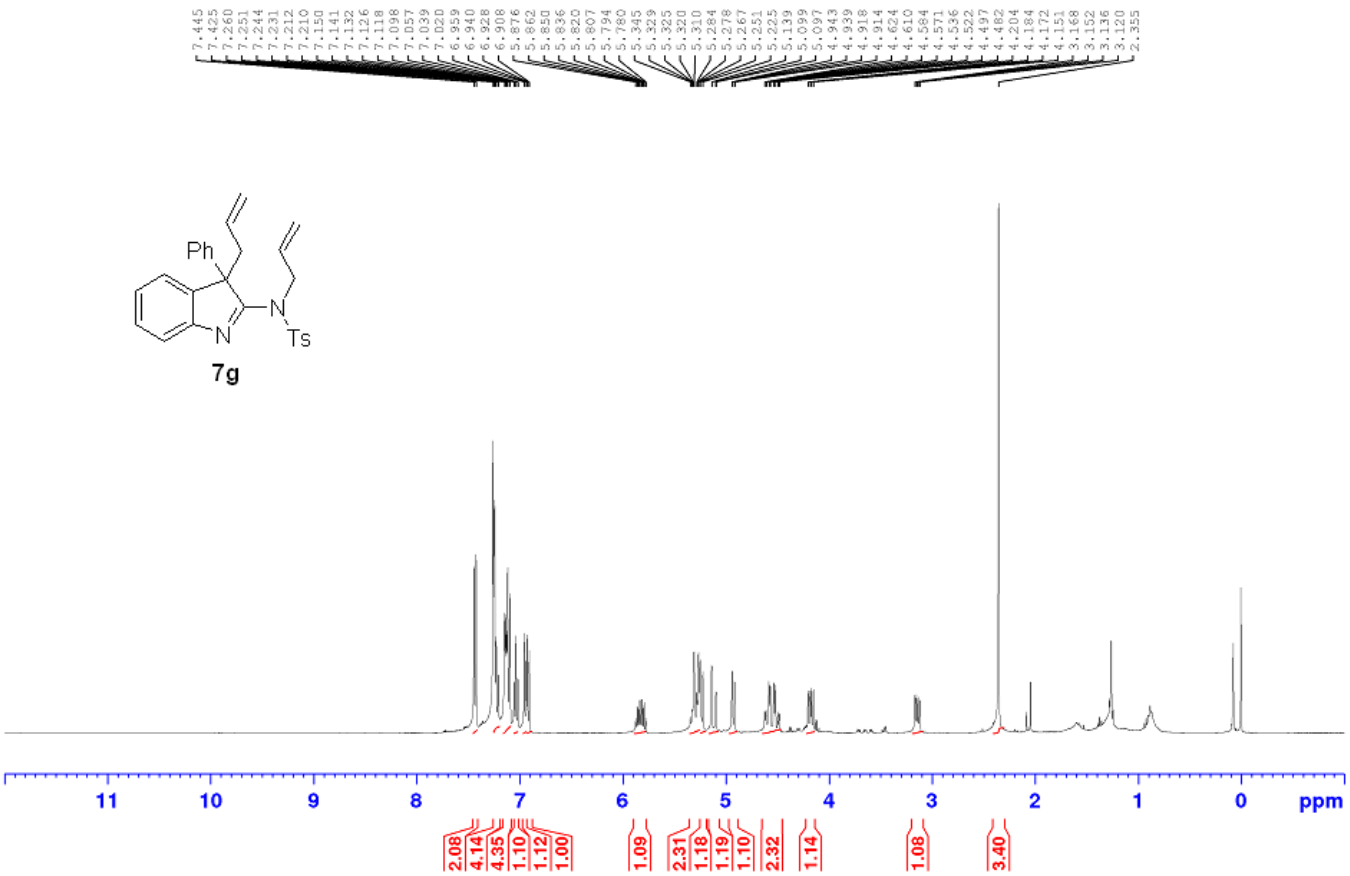


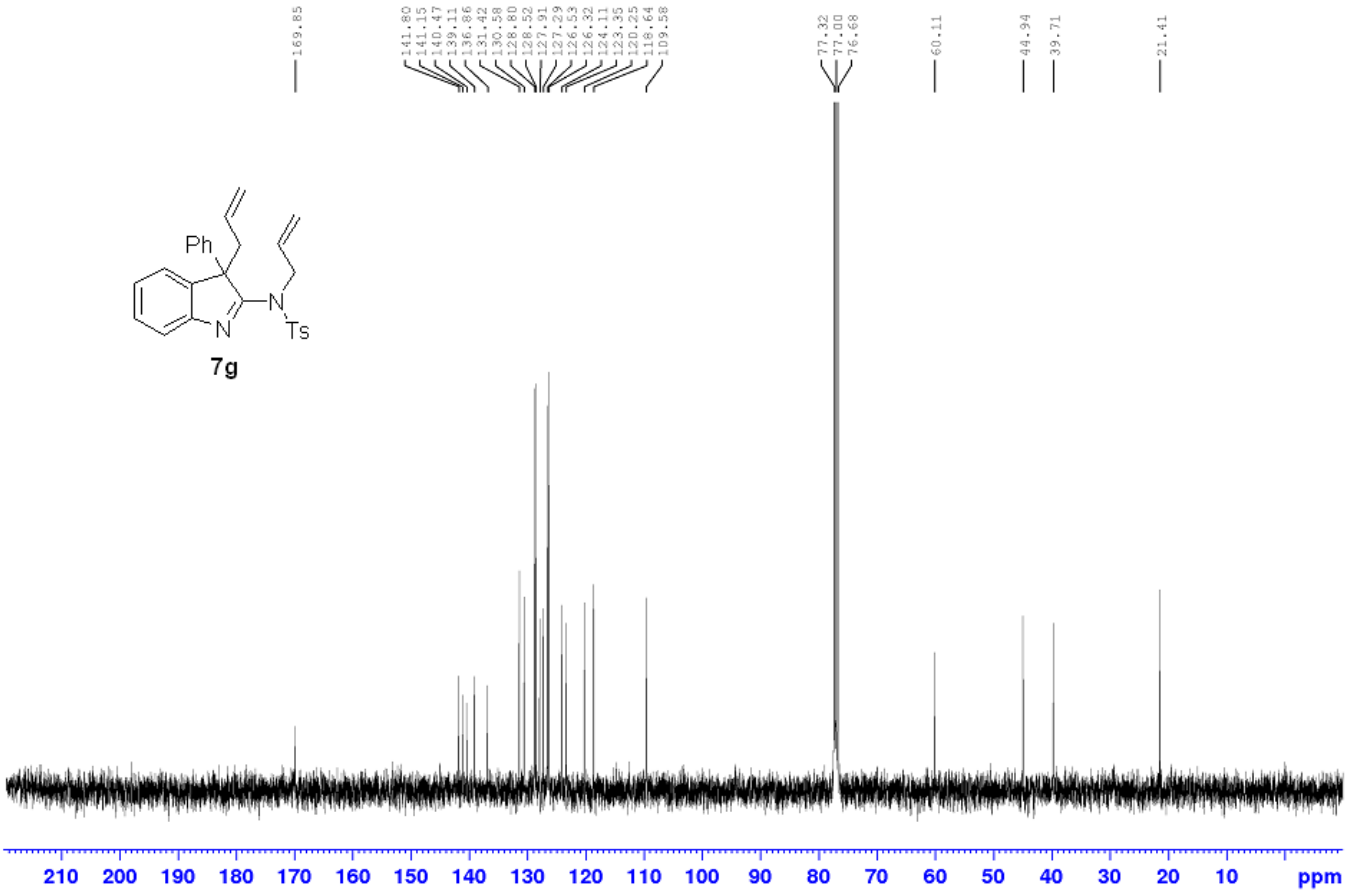
4-Methyl-*N*-(3-phenyl-1*H*-indol-2-yl)benzenesulfonamide (7f)



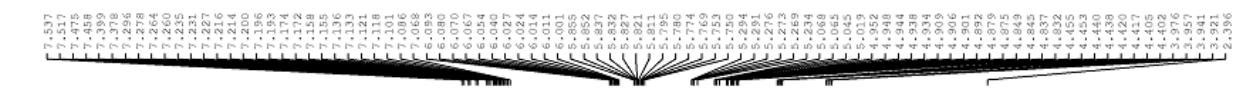


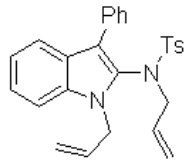
_N_-Allyl-_N_-(3-allyl-3-phenyl-3_H_-indol-2-yl)-4-methylbenzenesulfonamide (7g)



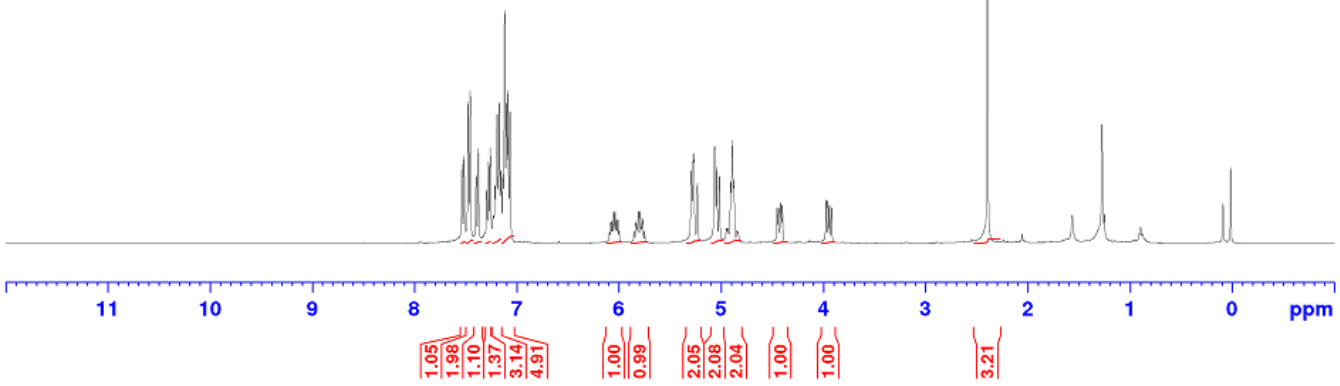


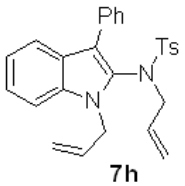
_N_-Allyl-_N_-(1-allyl-3-phenyl-1_H_-indol-2-yl)-4-methylbenzenesulfonamide (7h)



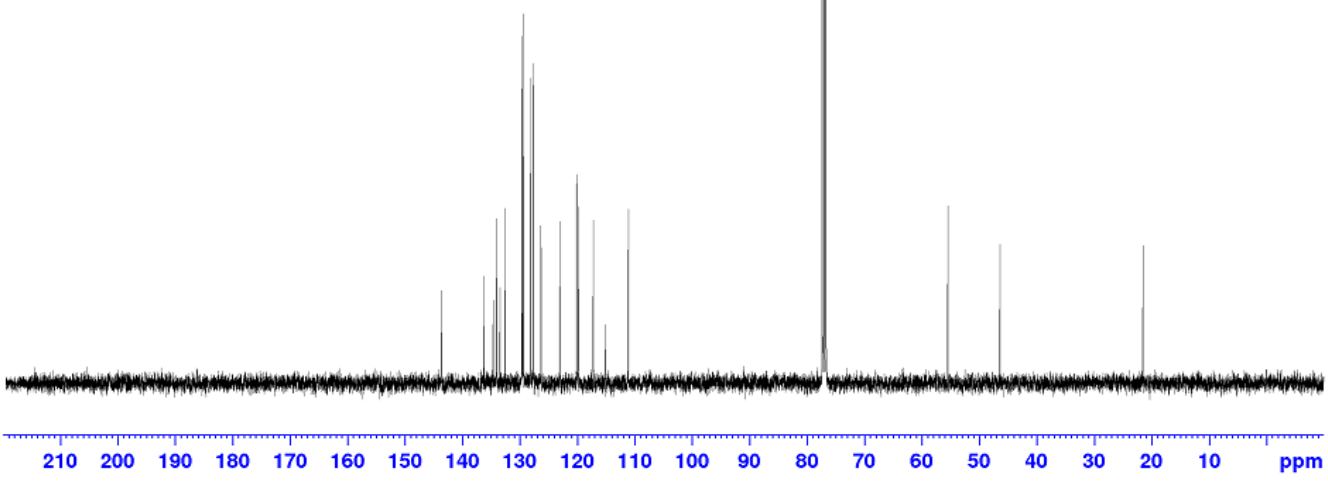


7h

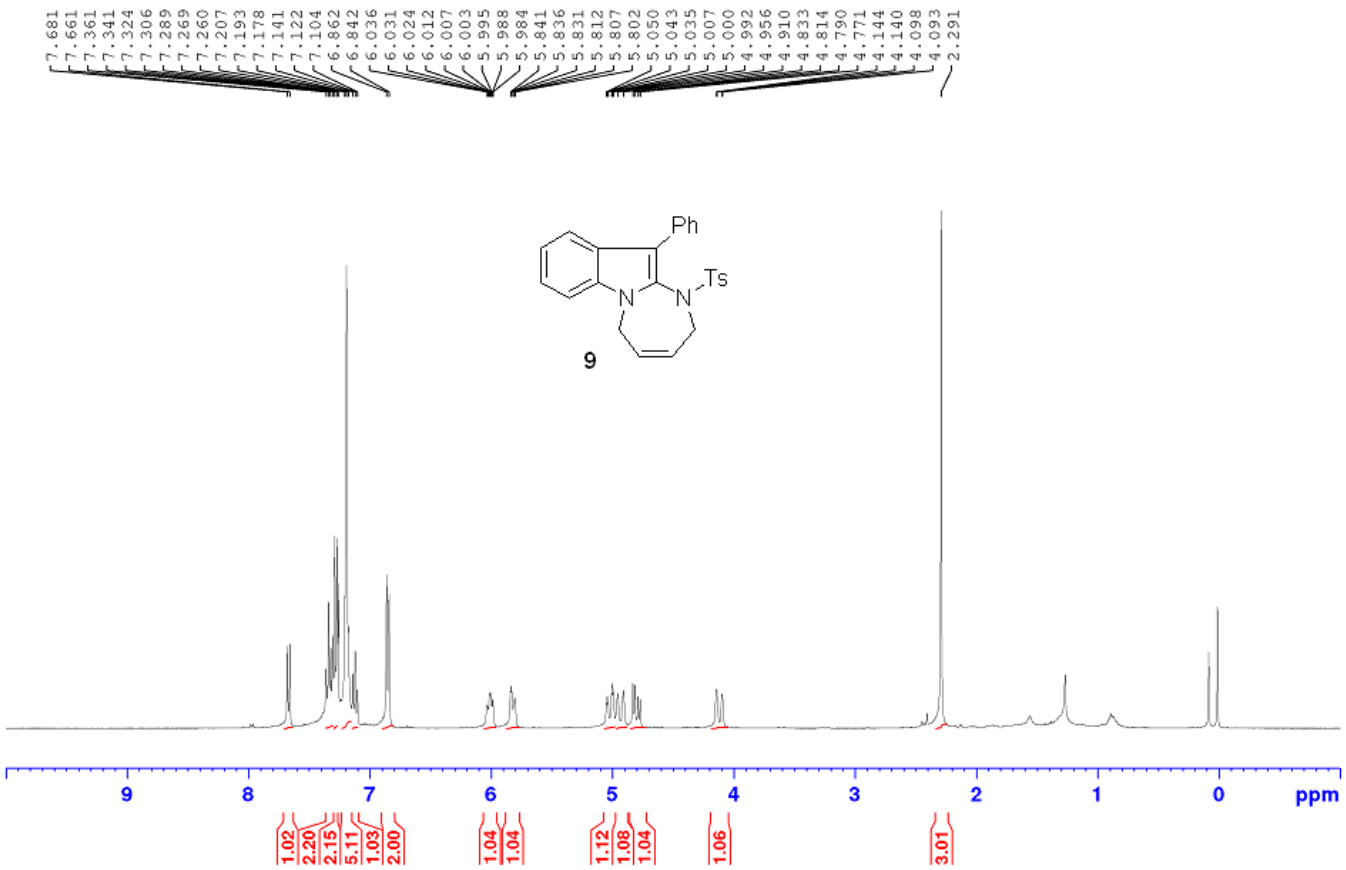


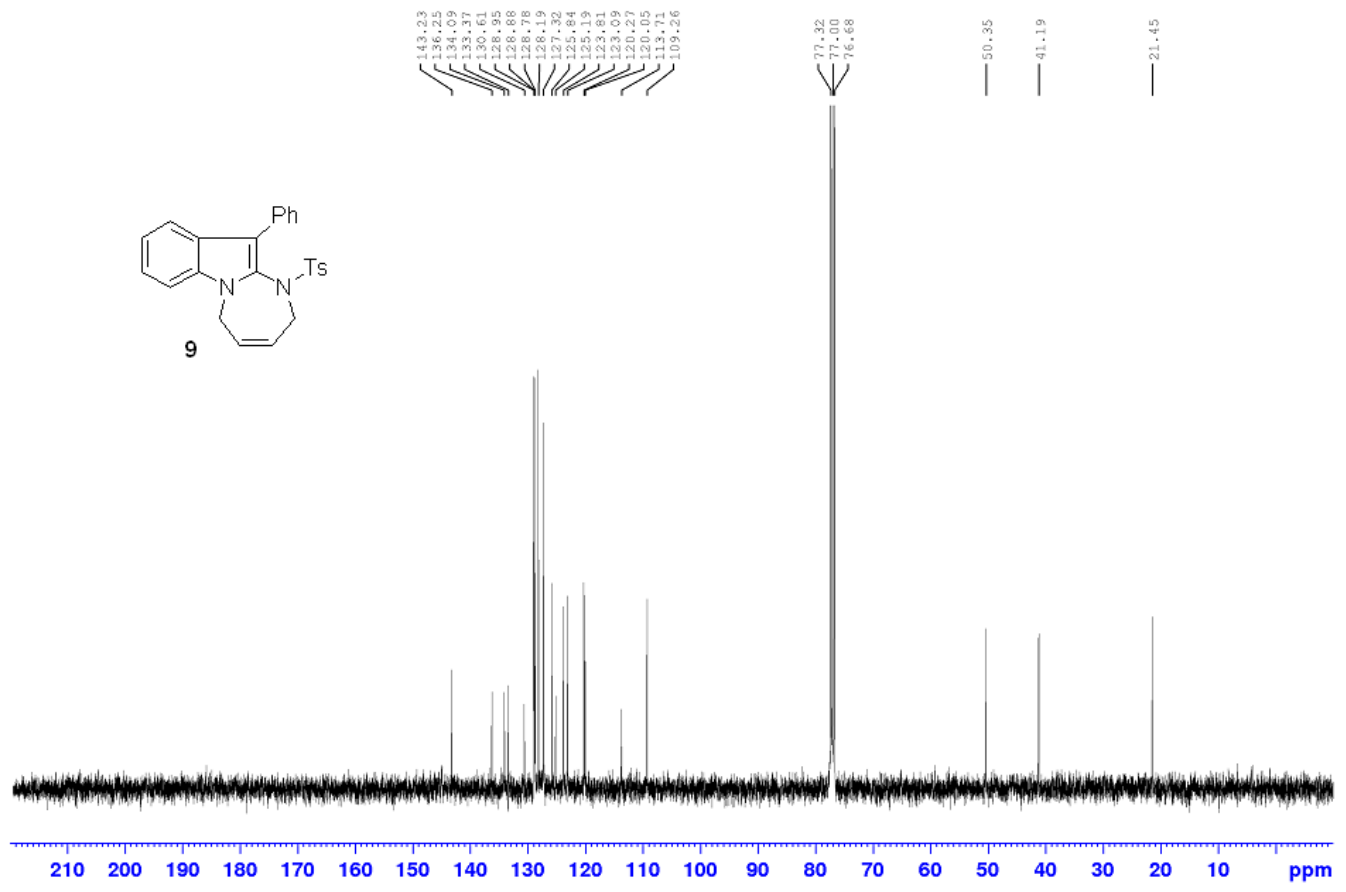


7h

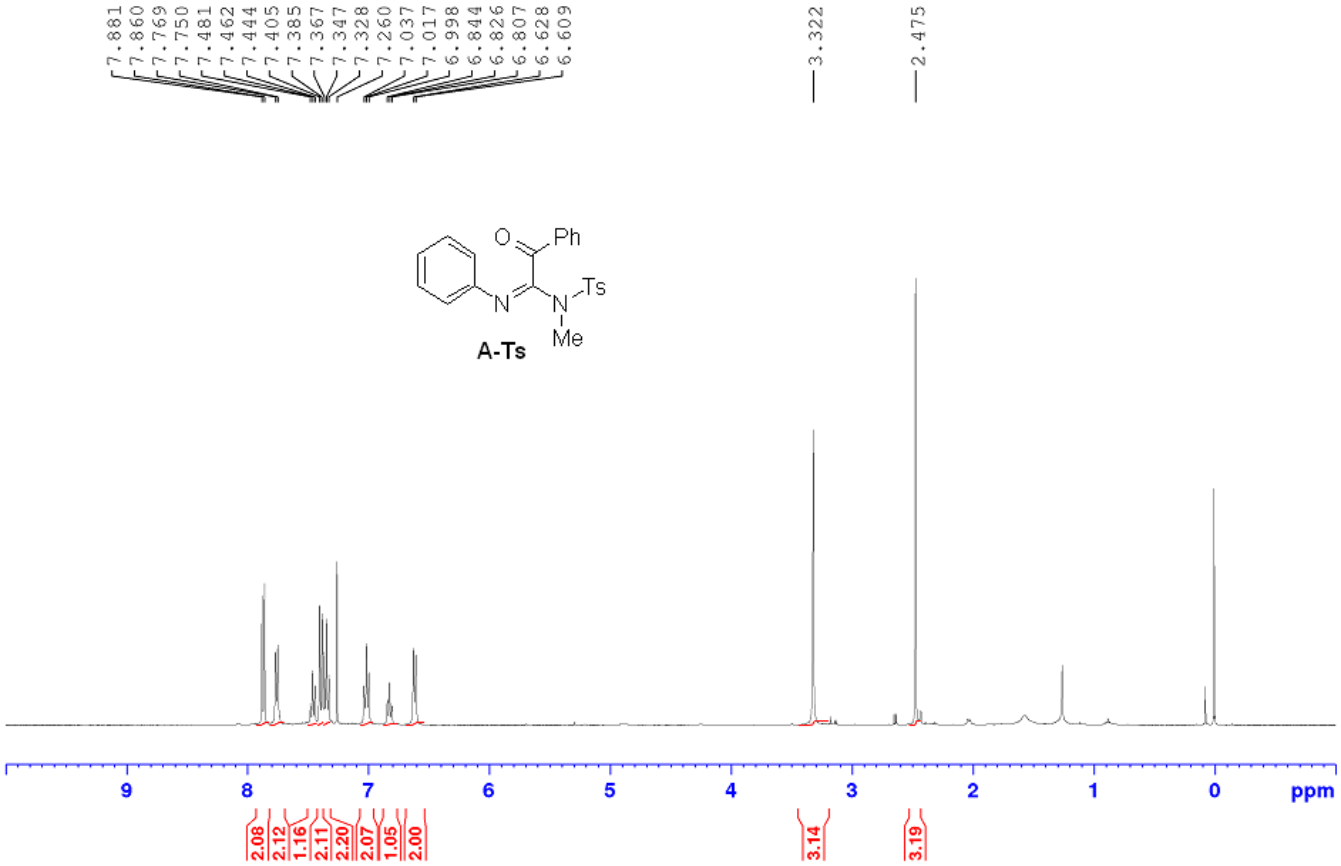


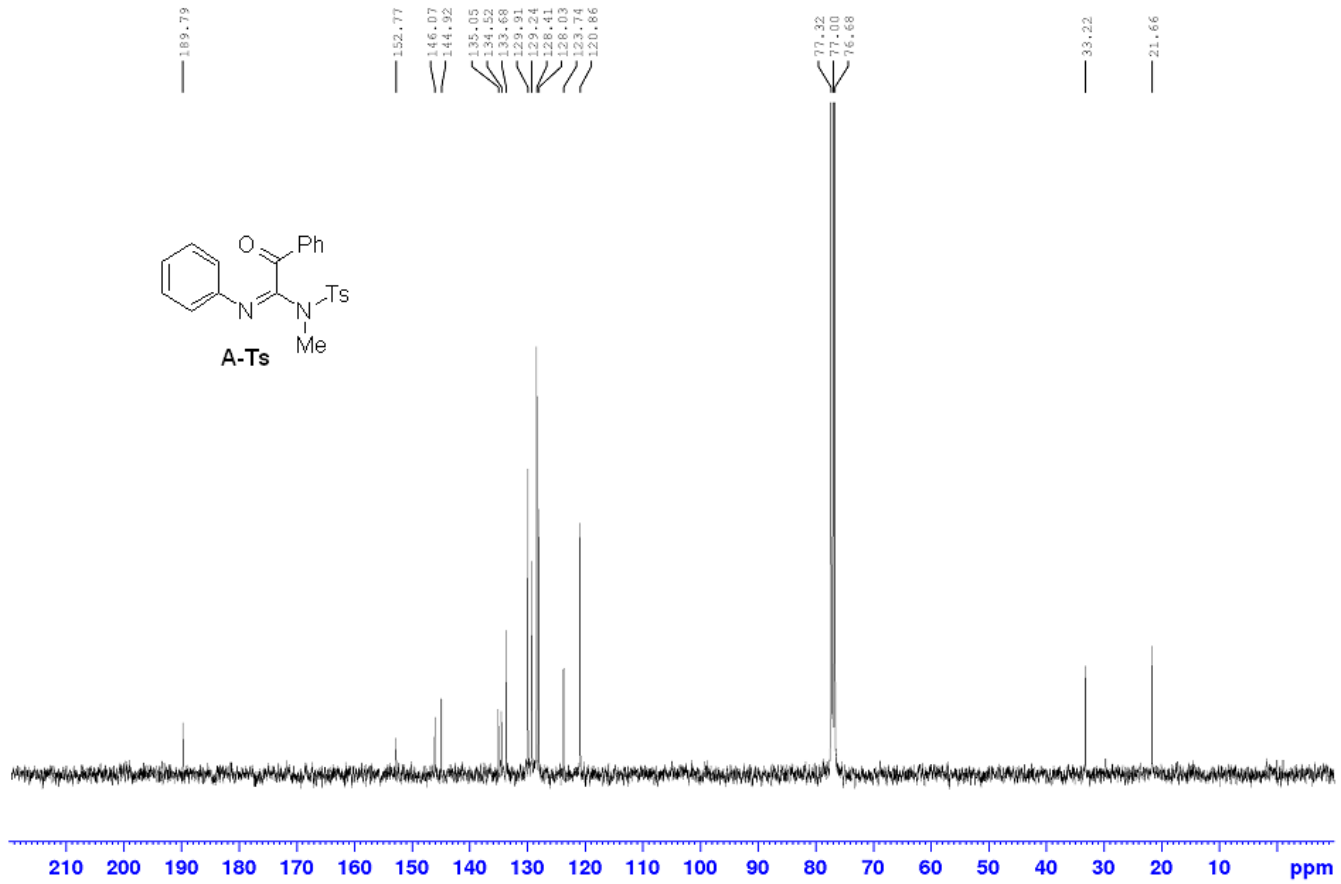
11-Phenyl-1-tosyl-2,5-dihydro-1*H*-[1,3]diazepino[1,2-*a*]indole (9)



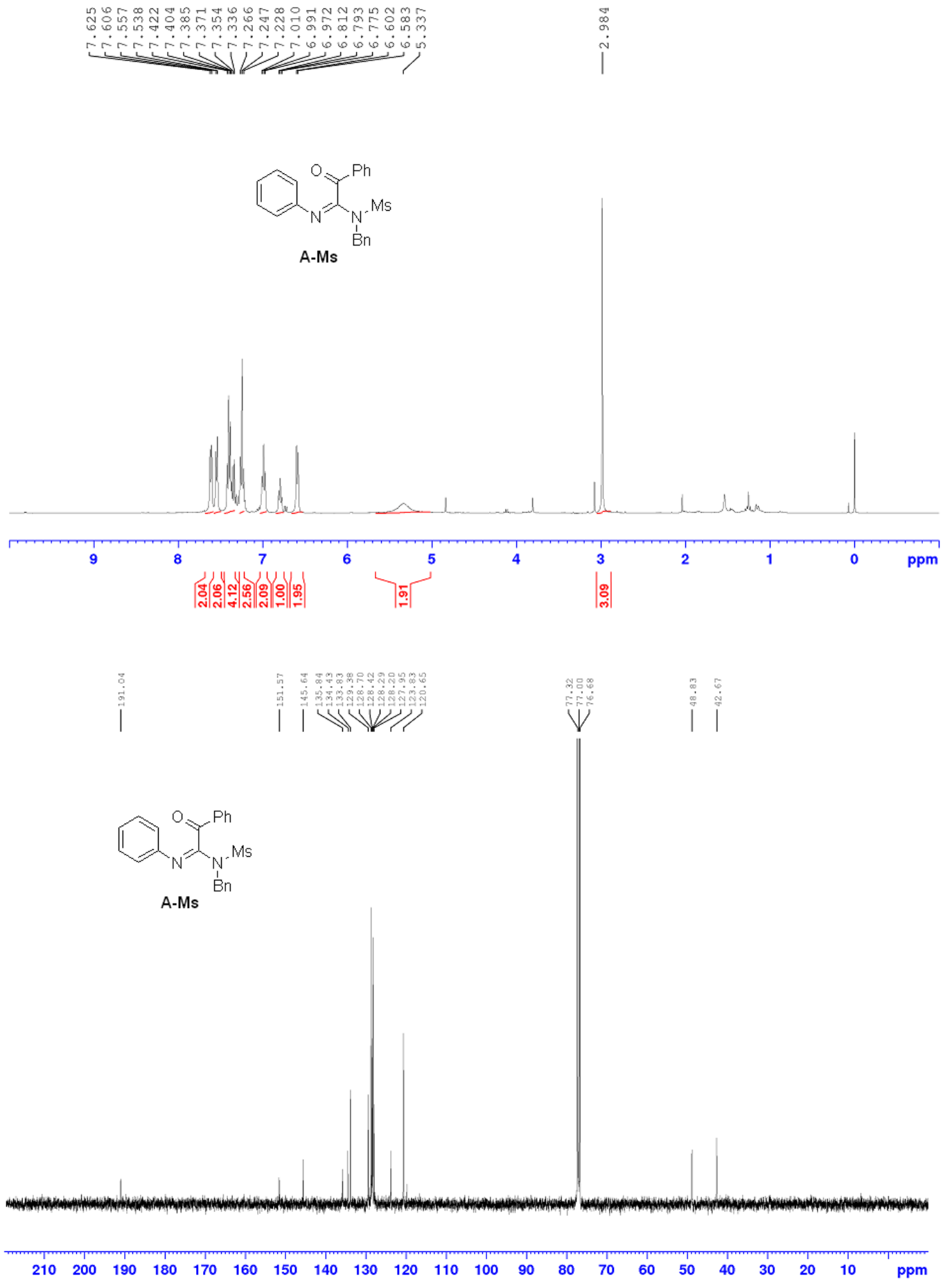


(*E*)-*N*-Methyl-2-oxo-*N*′,2-diphenyl-*N*-tosylacetimidamide (A-Ts)

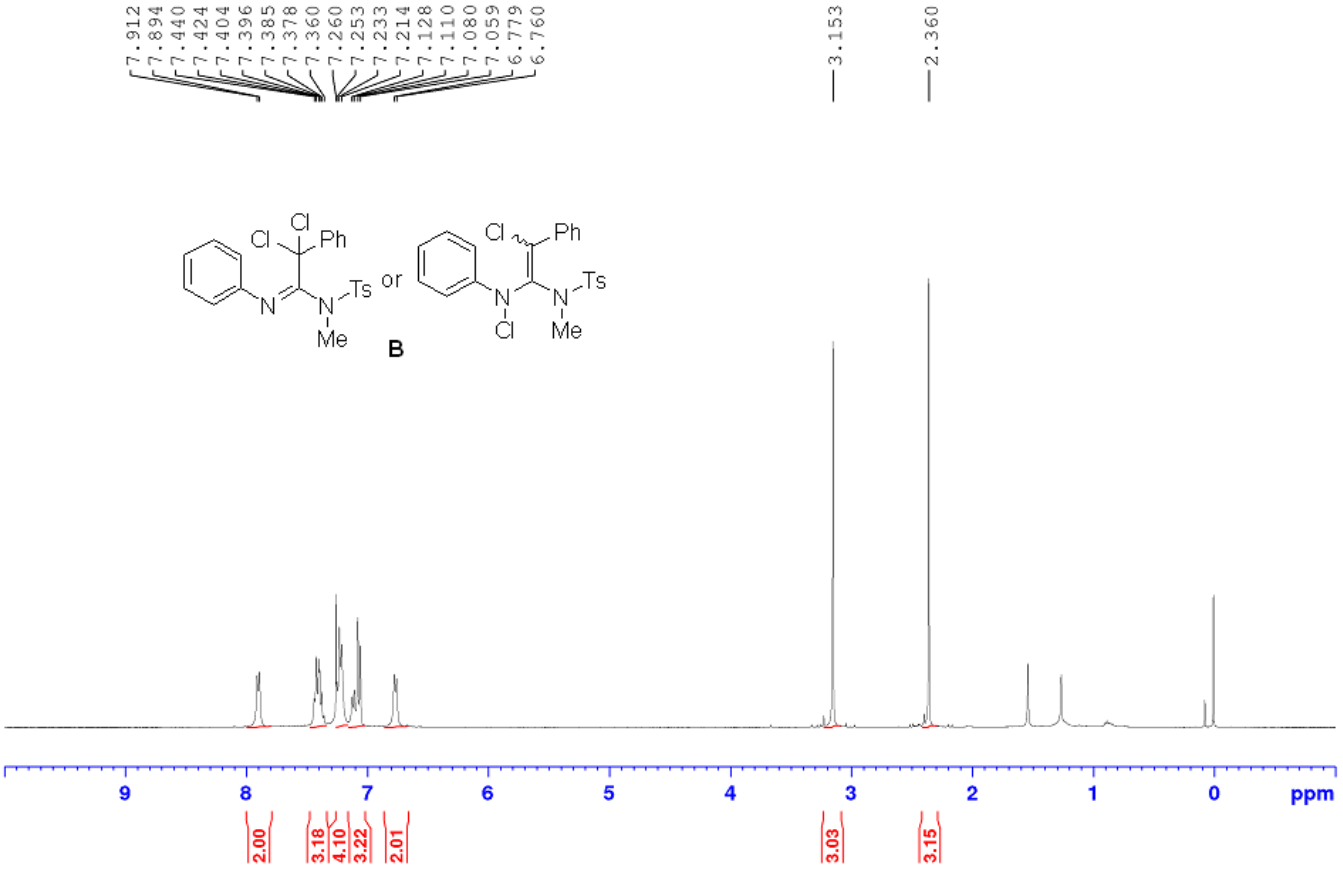


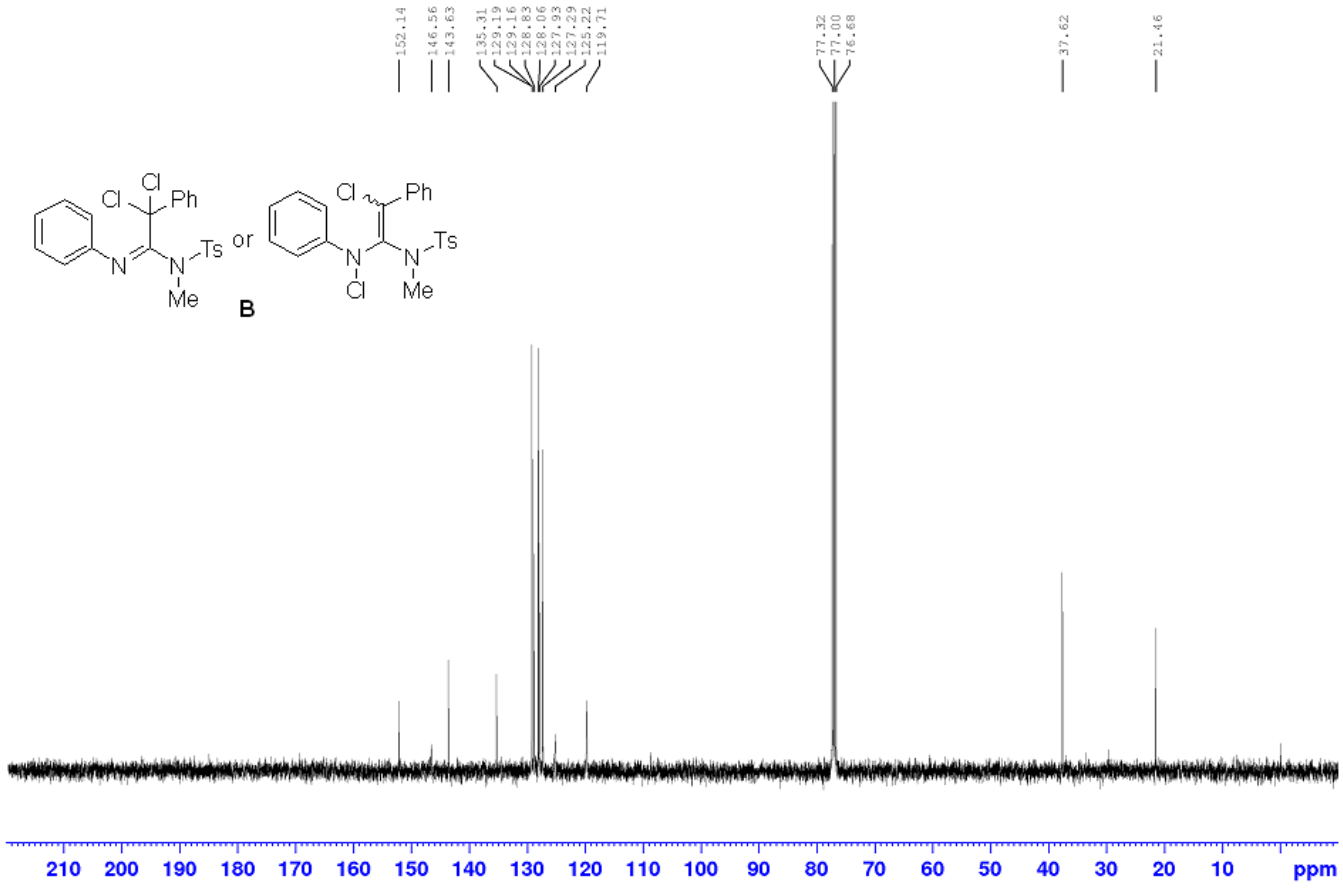


(*E*)-*N*-Benzyl-*N*-(methylsulfonyl)-2-oxo-*N*′,2-diphenylacetimidamide (A-Ms)

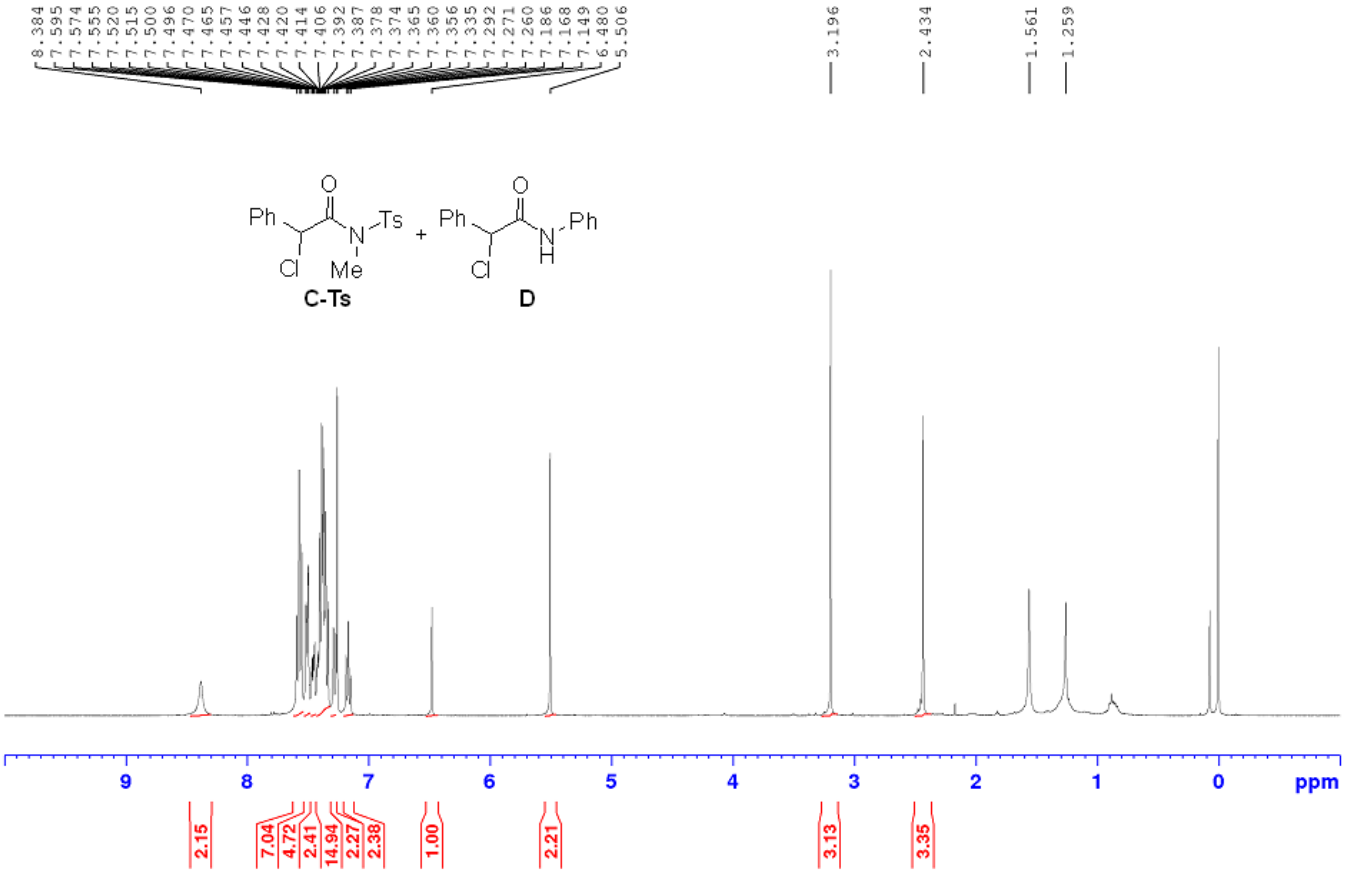


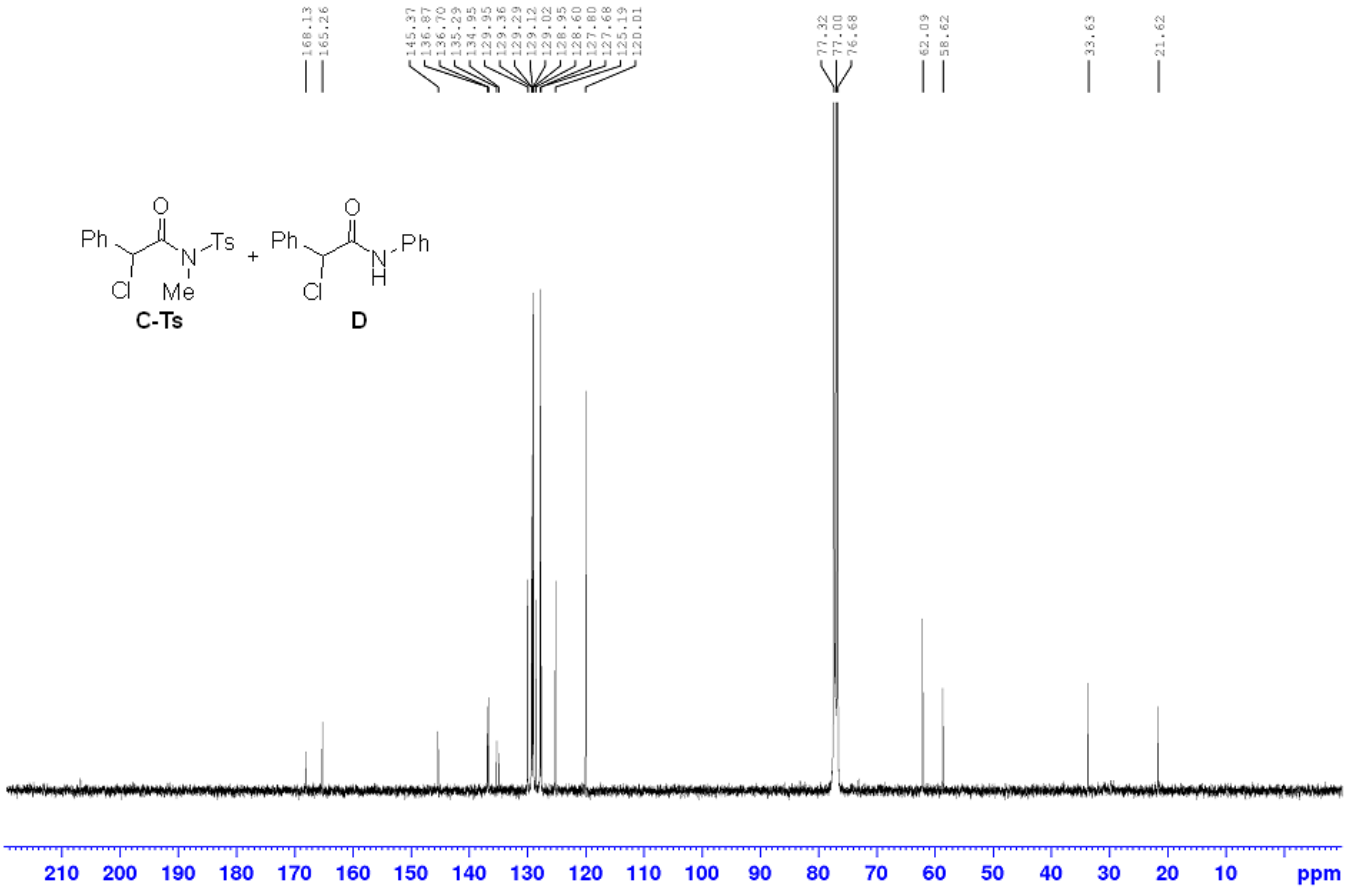
(*E*)-2,2-Dichloro-*N*-methyl-*N*′,2-diphenyl-*N*-tosylacetimidamide or *N*-(2-chloro-1-(chloro(phenyl)-amino)-2-phenylvinyl)-*N*,4-dimethylbenzenesulfonamide (B)





2-Chloro-*N*-methyl-2-phenyl-*N*-tosylacetamide (C-Ts) & 2-Chloro-*N*,2-diphenylacetamide (D)





***N*-(1-Chloro-2-phenylvinyl)-*N*,4-dimethylbenzenesulfonamide (E)**